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ANNUAL REPORTS
ON THE
PROGRESS OF CHEMISTRY.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1928.

ISSUED BY THE CHEMICAL SOCIETY.

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Vol. XXV.

LONDON:
THE CHEMICAL SOCIETY
1929.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	FULL TITLE.
A.	Abstracts in Journal of the Chemical Society.
A.	British Chemical Abstracts,* Section A.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Acad. Sci. Fennicae	Annales Academia Scientiarum Fennicae.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Reports	Annual Reports of the Chemical Society.
Apoth.-Ztg.	Apotheker-Zeitung.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti (Rendiconti, Memorie) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
B.	British Chemical Abstracts,* Section B.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Sächs. Ges. Wiss.	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften (math.-phys. Klasse).
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Boll. Chim. farm.	Bolletino Chimico farmaceutico.
Brit. Assoc. Reports	Reports of the British Association for the Advancement of Science.
Bul. Soc. chim. România	Buletinul Societătei de Chimie din România.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Inst. Phys. Chem. Res. Tokyo	Bulletin of the Institute of Physical and Chemical Research, Tokyo.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.

*** The year is not inserted in references to 1928.**

Abbreviated Title.	FULL TITLE.
Cellulosechem.	Cellulosechemie.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Védu a Průmysl."
Chem. News	Chemical News.
Chem. Reviews	Chemical Reviews.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Chim. et Ind.	Chimie et Industrie.
Chinese J. Physiol.	Chinese Journal of Physiology.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
D.S.I.R., H.M. Stat. Office	Department of Scientific and Industrial Research, His Majesty's Stationery Office.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Deut. med. Wochenschr.	Deutsche medizinische Wochenschrift.
Fermentforsch.	Fermentforschung.
Gazzetta	Gazzetta chimica italiana.
Giorn. Chim. Ind. Appl.	Giornale di Chimica Industriale ed Applicata.
Helv. Chim Acta	Helvetica Chimica Acta.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Indian J. Physics	Indian Journal of Physics.
J.	Journal of the Chemical Society.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Ind. Moscow	Journal of Chemical Industry, Moscow.
J. Chim. phys.	Journal de Chimie physique.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Ind. Hygiene	Journal of Industrial Hygiene.
J. Inst. Metals	Journal of the Institute of Metals.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. S. African Chem. Inst.	Journal of the South African Chemical Institute.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Chem. Japan	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
Kgl. Danske Videnskap. Selsk. math.-fys. Medd.	Kongelige Danske Videnskapernens Selskab, mathematisk-fysiske Meddelelser.

Abbreviated Title.	FULL TITLE.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kunglig-Vetenskapsakademiens Nobel-Institut.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nach. Ges. Wiss. Göttingen.	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
Neue Jahrb. Min.	Neue Jahrbuch für Mineralogie.
Norsk Geol. Tidsskrift	Norsk Geologisk Tidsskrift, Oslo.
Norsk. Vid. Akad.	Skrifter utgitt av det Norske Videnskaps-Akademi i Oslo. I, Matem.-Naturvid. Klasse.
Notiz. chim.-ind.	Notiziario chimico-industriale.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Physiol. Abs.	Physiological Abstracts.
Physiol. Reviews.	Physiological Reviews.
Plant Physiol.	Plant Physiology.
Proc. Amer. Acad. Arts Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. Indiana Acad. Sci.	Proceedings of the Indiana Academy of Sciences.
Proc. Indiana Chem. Soc.	Proceedings of the Indiana Chemical Society.
Proc. Iowa Acad. Sci.	Proceedings of the Iowa Academy of Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. New South Wales	Proceedings of the Royal Society of New South Wales.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Pub. Fac. Sci. Univ. Masaryk	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Prírodovèdeckon Facoulton Masarykovy University).
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. gén. Colloid.	Revue générale des Colloïdes.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Rep. Tôhoku Imp. Univ.	Science Reports, Tôhoku Imperial University.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.

Abbreviated Title.	FULL TITLE.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Ukraine Chem. J.	Ukrainian Chemical Journal.
U. S. Pub. Health Rep.	United States Public Health Reports.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Krist.	Zeitschrift für Krystallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zentr. Min. Geol.	Zentralblatt für Mineralogie, Geologie, und Paläontologie.

ERRATA.

VOL. XXIV, 1927.

Page.	Line.	
151	7*	*for* "(*I*, ↷)" *read* "(*I*, →)."
151	6*	*for* "(*T*, →)" *read* "(*T*, ↷)."
354	4	*for* "Subramanian, V., 221, 223" *read* "Subrahmanyan, V., 221. Subramaniam, V., 223."

* From bottom.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

THE large output of research in this branch of the subject has been maintained and, in accordance with the practice of previous years, this Report is confined to a few topics which have been brought into prominence during the year and have not been reported upon for some time.

Infra-red Spectroscopy.

Four important papers [1] on this subject have been published by Sir R. Robertson and J. J. Fox (one of them in collaboration with E. S. Hiscocks). The first part of the investigation consisted of an elaborate study of the conditions necessary for ensuring success in the work, the object of which was to measure the infra-red absorption of ammonia, phosphine, and arsine. The source of energy employed was a Nernst filament, backed by a concave mirror and enclosed in an asbestos housing. It was supplied with a current of 1 amp. at 110 volts from a battery of accumulators, as the supply from the mains was not sufficiently steady. An account is given of the difficulties encountered and the masterly way in which they were overcome: the calibration of the spectrometer, correct alinement of the observation tubes, electromagnetic and mechanical shielding of the galvanometer, and the method of attachment of the leads were all very carefully carried out in order to ensure high accuracy of the results. The care expended on this part of the work is made evident by the fact that the bismuth–silver 20-junction thermopile was shielded to protect it from the effect of adiabatic compression of the air of the laboratory, *e.g.*, by the sudden closing of a door.

The method of observation used for the most part in these investigations was to bring alternately into the optical path two tubes, the one containing gas and the other gas-free. This resulted in speedier and more accurate working than the alternative method of using one tube only and evacuating it to determine the emission of the Nernst filament. Two tubes, 100 and 450 mm. long, were employed, according as strong or weak bands were being explored. Interesting details are given for the calibration of the wave-length drum of the spectrometer for prisms of rock-salt, quartz, and fluorite, and special care was taken to allow for the effect of temperature on the refractive indices of these materials.[2] The gases used were prepared with the utmost regard for purity. The resolution effected was not sufficient to show fine structure below 2·2 μ with the quartz prism: bands were partly resolved from 2·2 μ (quartz), 4 μ (fluorite), and 5 μ (rock-salt), and the fine structure was revealed in the bands above 3 μ (quartz), 6 μ (fluorite), and 8 μ (rock-salt). In the case of unresolved bands, the centre near the peak was taken as the oscillation frequency. The partly resolved bands show three peaks, of which the centre one was taken as the oscillation frequency, the side peaks also being evaluated. In the case of the fully resolved bands, the positions of the rotation maxima imposed on the oscillation band are given. The results are calculated in terms of percentage absorption against wave number, and the spectra of the three compounds are compared.

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[1] *Proc. Roy. Soc.*, 1928, [*A*], **120**, 128, 141, 161, 189; **A.**, 1073.

Ammonia has the most complicated spectrum, but all three gases have in common a main sequence of harmonic bands (I, II, . . . V or VI), ammonia has a second sequence (C, D, . . .) not present in phosphine or arsine, a faint sequence (a, b, . . .), and bands at 4·05 and 10·55 μ. Phosphine and arsine have also a second sequence (A′, B′, . . . and A″, B″, . . .) and a sequence (α, β, . . .) not present in ammonia. The main bands I—VI are nearly in harmonic sequence and their intensity in general decreases towards the visible region of the spectrum. These bands are all of the same type characterised by an intense zero (Q) branch with less intense side branches (P and R). The ammonia band at 10·55 μ has the unique feature of possessing two Q branches close together. Beer's law ($I = I_0\varepsilon^{-kp}$) is obeyed for all the gases at lower pressures in the case of the fine structure bands, but deviations occur, particularly at atmospheric pressure, and these are, no doubt, connected with the fusion of the bands.

Nearly constant ratios are found to exist between the vibration numbers of the members of the main sequence common to the three gases, and the second sequence (A′, B′, etc.) in phosphine and arsine has a common ratio similar to that in the main series. There are thus certain degrees of freedom common to the three gases. The molecular moments of inertia for the three compounds are calculated from the mean spacing differences determined from the fine structure of some of the bands, and are compared with the values given by the classical energy relation for three degrees of freedom in the following table :

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[2] *Ann. Reports*, 1927, **24**, 14.

	$J_1 \times 10^{40}$ (c.g.s.) from band structure.	$J_2 \times 10^{40}$ (c.g.s.) from energy relation.	J_2/J_1.
NH_3	2·78	3·49	1·26
PH_3	4·78	6·24	1·30
AsH_3	5·53 or 6·51	8·28	1·27 or 1·49

The fairly constant ratio in the last column indicates that the factor used with kT in the classical equation should be less than 3/2.

The results may be taken to support a tetrahedral model for the molecule of ammonia, but appear to indicate that the oscillations are greater in number than can be accounted for by consideration of valency bonds alone. If the molecule of ammonia be considered as a tetrahedron (and it is unnecessary to place the nitrogen atom at any great distance from the plane of the hydrogen atoms), there appear to be six possible modes of vibration : (1) nitrogen against the plane of the hydrogen atoms (*i.e.*, along a line directed towards the centre of gravity of the model), (2) nitrogen against one hydrogen atom, (3) hydrogen perpendicular to a line joining it to the centre of gravity of the model, (4) nitrogen as in (3), (5) the molecule rotating about its centre of gravity, and (6) the molecule rotating about an axis through the line joining the nitrogen atom to the centre of gravity. Plane models are possible, but more difficulties are encountered with these than with the tetrahedral model. These considerations apply likewise to phosphine and arsine. Work on the infra-red absorption of the N–H linking in substituted ammonias has been carried out by J. W. Ellis [3] and by E. Hulthèn and S. Nakamura.[4]

A. A. Levin and C. F. Meyer [5] have studied the infra-red absorption spectra of acetylene, ethylene, and ethane between 2 and 15 μ. Each gas shows a characteristic structure for its vibrational-rotational bands. Acetylene shows three main absorption regions which were resolved into lines which are alternately intense and faint, and have the same average spacing in the three bands. The molecular moment of inertia of acetylene calculated from the spacing of the fine structure of the principal bands is in agreement with that obtained from the classical theory of energy on the assumption of a linear molecular structure. Ethylene shows seven regions of absorption. Two of these lack Q branches, one shows a strong Q branch, and the other four show sharp Q branches together with P and R branches. Ethane shows bands each consisting of a single succession of absorption maxima. An expression for the shape of an infra-red absorption line has been developed by D. M. Dennison,[6] who shows that the absorption coefficient may be expressed by means of two damping curves involving the number of molecules per unit volume, the temperature, and the effective diameter of the molecule. The formulæ are applied to the case of hydrogen chloride, and a value of $10{\cdot}8 \times 10^{-8}$ cm. is obtained for its effective diameter. The infra-red emission spectrum of hydrogen has been examined,[7] and 6 higher members of the Paschen series with wave-lengths in accordance with the Bohr theory have been observed.

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[3] *J. Amer. Chem. Soc.*, 1927, **49**, 347; 1928, **50**, 685; **A.**, 1927, 291; 1928, 458.

[4] *Nature*, 1927, **119**, 235; **A.**, 1927, 185.

[5] *Proc. Nat. Acad. Sci.*, 1927, **13**, 298; **A.**, 1927, 918; *J. Opt. Soc. Amer.*, 1928, **16**, 137; **A.**, 570.

Rotatory Dispersion.

An attempt [8] has been made to decide the vexed question of the spatial configuration of optically active molecules by reference to rotatory dispersion curves and temperature-rotation curves. The authors of this attempt reject as incomplete the view that anomalous rotatory dispersion is due to an infra-red rotatory electron and an ultra-violet rotatory electron of the same sign,[9] and also the view that it is due to two ultra-violet rotatory electrons of opposite sign,[10] and have put forward the theory that it is due to " one or more rotations of electronic origin in the ultra-violet and a rotation of molecular origin, due to atomic oscillations, in the infra-red." It is considered that the partial rotation due to the infra-red term, although small in the visible region, is of great importance, since, being of molecular origin, its sign is of necessity the same as that of the molecular configuration. The conventions of nomenclature here are important: an infra-red term of lævorotatory molecular origin will contribute a dextrorotatory dispersion to the rotatory power, since the latter of necessity changes sign on crossing a band, and the visible and accessible region of the spectrum is on the high-frequency side of the infra-red band. Nevertheless—since the greater part of the rotatory power in the region of the spectrum accessible to experimental observation is due to the ultra-violet rotatory electron system which, owing to the fact that it absorbs energy on the high-frequency side of the accessible region of the spectrum, contributes a partial rotation of its own sign to the total rotatory power—a molecular structure which contributes a lævorotatory term (one of negative sign) to the dispersion equation is said to possess a dextro-configuration. Various possible cases are considered, the initial treatment being similar to work already published[11] except that, in this instance, the visible region of the spectrum lies between the absorption bands instead of on the low-frequency side of them. The authors accept the Drude equation as the basis of their theoretical arguments, and by consideration of one infra-red and two ultra-violet terms they are led to an interesting extension of existing theory when the ultra-violet terms are of opposite sign and the one of highest frequency has a sign opposite to that of the infra-red term, *i.e.*, when $\alpha = k_1/(\lambda^2 - \lambda_1^2) - k_2/(\lambda^2 - \lambda_2^2) - k_3/(\lambda^2 - \lambda_3^2)$ and $\lambda_1 < \lambda_2 < \lambda_3$. In this case, the dispersion curve can cross the axis only in one way, that is, when $d\alpha/d\lambda$ has the same sign as the ultra-violet term of highest frequency. When this occurs, the anomalies (maximum on the curve and point of inflexion) must of necessity lie in the region of rotatory power of this sign. This case is illustrated above, where the full curve EF

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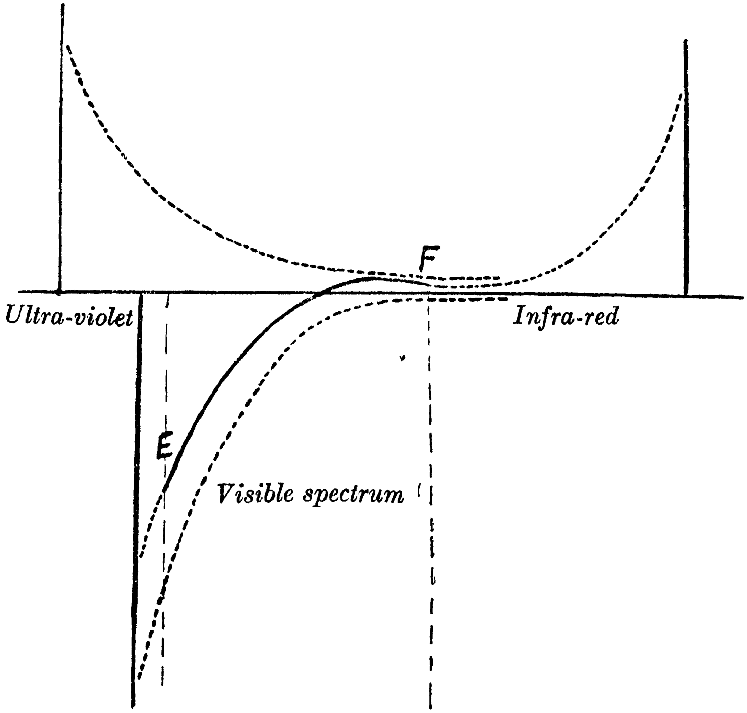
[6] *Physical Rev.*, 1928, [ii], **31**, 503; **A.**, 571.

[7] A. H. Poetker, *ibid.*, 1927, [ii], **30**, 418; **A.**, 1927, 1117; *Nature*, 1927, **119**, 123; **A.**, 1927, 177.

[8] C. E. Wood and S. D. Nicholas, *J.*, 1928, 1671, 1696, 1712, 1727; C. E. Wood, A. E. Chrisman, and S. D. Nicholas, *ibid.*, p. 2180.

[9] R. W. Wood, " Physical Optics," Macmillan, 1919 ed., p. 492.

[10] T. M. Lowry and R. O. Cutter, *J.*, 1925, **127**, 604.



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[11] *Ann. Reports*, 1924, **21**, 3.

is the sum of the partial rotations represented by the dotted curves.

Under these conditions, Lowry's criterion for the limiting condition for anomaly [12] requires modification. Whereas, on the older view, k_1 was required to be greater than k_2 when λ_1 was less than λ_2 for anomaly to occur, the present theory extends the region of variability of k_1 to include the case of its equality to k_2 without causing the disappearance of the anomaly, since the curve is made to cross the axis even when $k_1 = k_2$ by the influence of the infra-red term, however small this may be. If the influence of the infra-red term is large, of course, k_2 may even appreciably exceed k_1 without causing the anomaly to disappear. It follows from this that *in all cases of anomalous dispersion the sign of the high-frequency term in the Drude equation is, regardless of its magnitude, opposite to that of the infra-red term, and hence the same as that of the configuration of the molecule.* Reference to the sign of the infra-red term thus becomes necessary for determining configuration only in cases of simple and complex but not anomalous dispersion. The term "simple" is here applied to dispersions which require only one ultra-violet term in the Drude equation.

It is considered that the infra-red term in the dispersion equation is due to the atomic tetrahedron about the asymmetric carbon atom, and that the ultra-violet terms are due to much lighter electronic tetrahedra similarly disposed. With eight electrons about the carbon (or other) atom, two tetrahedra would be obtained which, when displaced in opposite directions in response to light waves, would give rise to anomaly in the region between the near ultra-violet and the infra-red basic frequencies, and possibly in the visible region; when displaced in the same direction would give rise to complexity but not to anomaly; and when displaced in the same direction and acting as a single tetrahedron, would give rise to simplicity of rotatory dispersion.

The above rule for determining configuration gives, when it can be applied, an absolute specification of configuration, and thus, for the first time, configurations of unrelated compounds may be compared, but the assignment of absolute space formulæ requires, in addition, a knowledge of the order of the deflexion of the four groups involved, and this is at present available only in the cases of homologous series and other classes of compound structurally related by synthesis. Many cases of this kind are reviewed by these investigators.

When anomaly is present, information regarding configuration may be obtained by a consideration of temperature–rotation curves.

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[12] *Ann. Reports*, 1914, **11**, 15.

After a detailed examination of the possible cases, these authors arrive at this conclusion, amongst others: that the configuration of a compound may be determined from a family of temperature–rotation curves by the following considerations: (*a*) the slope of the curve, $d\alpha/dT$, where it crosses the axis of zero rotation is positive for a compound of *d*-configuration if the maxima on the curves are on the high-temperature side of the anomalous region, and (*b*) the maxima move from high to low temperatures as the wave-length increases. These considerations are reversed if the region of anomaly is on the high-temperature side of the maxima, and the conditions for a compound of *l*-configuration are, of course, mirror images of those for compounds of *d*-configuration.

The validity of the Drude equation has been questioned by T. Bradshaw and G. H. Livens,[13] who have applied an equation (previously derived by one of them [14]) to the rotatory dispersion of quartz. Lowry fitted his first series of data [15] by means of the equation

$$\alpha = A_1/(\lambda^2 - \lambda_1^2) + A_2/(\lambda^2 - \lambda_2^2) + A_3/\lambda^2 \quad . \quad . \quad (1)$$

with $\lambda_1^2 = 0{\cdot}010627$; $\lambda_2^2 = 78{\cdot}22\ \mu^2$.

His later, more accurate readings [16] between λλ 2·5170 and 0·2280 μ compelled him to modify his formula to

$$\alpha = A_1'/(\lambda^2 - \lambda_1^2) + A_2'/(\lambda^2 - \lambda_2^2) - A_3' . \quad . \quad . \quad (2)$$

with $\lambda_1^2 = 0{\cdot}0127493$; $\lambda_2^2 = 0{\cdot}000974\ \mu^2$;

so that λ_2 is now right down in the very short ultra-violet region of the spectrum instead of in the long infra-red region, and the effect of the infra-red term is replaced by a constant.

Neither of these formulæ, however, represents the results obtained by J. Duclaux and P. Jeantet [17] for the region between λλ 0·3086 and 0·185398 μ, and, furthermore, the constant term in Lowry's second equation is improbable since it cannot be reconciled with any theory of dispersion. Bradshaw and Livens have fitted all these observations by means of the formula

$$\alpha = \frac{845{\cdot}694}{\lambda^2 - \lambda_1^2} - \frac{0{\cdot}40235}{(\lambda^2 - \lambda_1^2)^2} - \frac{838{\cdot}4320}{\lambda^2 - \lambda_2^2} - \frac{0{\cdot}1331233}{(\lambda^2 - \lambda_2^2)^2} + \frac{43{\cdot}05794}{\lambda^2 - \lambda_3^2} + \frac{2119{\cdot}117}{(\lambda^2 - \lambda_3^2)^2} \quad . \quad . \quad . \quad (3)$$

where $\lambda_1^2 = 0{\cdot}01274912$, $\lambda_2^2 = 0{\cdot}01208000$, $\lambda_3^2 = 80\ \mu^2$, and α is in degrees per mm.

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[13] *Proc. Roy. Soc.*, 1929, [*A*], **122**, 245.

[14] G. H. Livens, *Phil. Mag.*, 1914, **27**, 994.

[15] *Phil. Trans.*, 1912, [*A*], **212**, 261.

[16] T. M. Lowry and W. R. C. Coode-Adams, *ibid.*, 1927, [*A*], **226**, 391; **A.**, 1927, 813.

[17] *J. Physique*, 1926, **7**, 200; **A.**, 1926, 886.

This formula fits the latest of Lowry's figures no better than formula (2), even although it contains nine adjustable constants as against five, but it possesses four advantages : (*a*) it has a more satisfactory theoretical basis; (*b*) it agrees with the figures of Duclaux and Jeantet to 1 part in 2000 parts (the accuracy claimed for the experimental figures) even at $\lambda = 0{\cdot}1850\ \mu$, whereas equation (2) shows divergences of 1 part in 200 parts; (*c*) it accounts for the practically constant effect of the infra-red absorption band; and (*d*) it does not introduce a new band in the extreme ultra-violet but only splits the old ultra-violet band into a close doublet.

The refractive and rotatory dispersions of monoethyl [18] and mono*iso*amyl [19] aspartates have been examined. In both cases the rotatory dispersion is anomalous and shows two inflexions similar to those in a refractive dispersion curve when passing through an absorption maximum, but the relation between the refractive and the rotatory dispersions of these esters is not apparent until the curve of $dn/d\lambda$ (where n denotes the refractive index) plotted against λ is compared with the rotatory dispersion curve. This behaviour is not exhibited by the dialkyl esters [20] of aspartic acid, which show normal rotatory dispersion. The anomalous behaviour of the monoalkyl esters is accounted for by internal salt formation.

The rotatory dispersion of tartaric acid as measured by T. M. Lowry and P. C. Austin [21] has been expressed by F. Bürki [22] by means of the equation $[\alpha] = A/\lambda^2\varepsilon^{a/\lambda^2} - B/\lambda^2\varepsilon^{b/\lambda^2}$, where $A, B, a,$ and b are constants. The validity of the conclusions of Lowry and Austin—that the addition of sufficient boric acid to aqueous solutions of tartaric acid " fixes " one of its hypothetical dynamic isomerides and thus, by eliminating one component of an alleged mixture of two substances of opposite rotation and unequal simple rotatory dispersion, produces simple rotatory dispersion in the solution—is rendered doubtful by the work of R. Descamps,[23] who has carried the dispersion measurements on these solutions to $\lambda = 0{\cdot}2537\ \mu$. He finds that these solutions, although exhibiting apparently simple rotatory dispersion in the visible region of the spectrum, manifest their real complexity when observations of rotatory power are pushed into the region of shorter wave-length. Similar measurements on solutions of molybdomalic complexes [24] show that these, too, exhibit complex rotatory dispersion. A considerable amount of work has been published on the rotatory dispersion of tartaric acid and the tartrates, both alone [25] and in the presence of other salts,[26] and the general conclusion seems to be that tartaric acid does exist in two forms in solution, possibly as simple and complex ions, or in some isomeric forms such as those postulated by Lowry and by Longchambon. Similar views for alkyl tartrates have been recently advanced by R. Lucas.[27]

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[18] M. L. Pagliarulo, *Atti R. Accad. Lincei*, 1927, [vi], **5**, 505; **A.**, 1927, 610.

[19] *Idem, ibid.*, **6**, 157; **A.**, 1928, 220.

[20] F. P. Mazza and G. Dello Jojo, *ibid.*, **5** 294; **A.**, 1927, 500; F. P. Mazza, *ibid.*, 1928, **7**, 148; **A.**, 460.

[21] *Phil. Trans.*, 1922, [*A*], **222**, 249; *A.*, 1922, ii, 418.

[22] *Helv. Chim. Acta*, 1928, **11**, 369; **A.**, 460.

[23] *Compt. rend.*, 1927, **184**, 453, 876; **A.**, 1927, 307, 409.

R. de Mallemann [28] has elaborated a theory of rotatory dispersion by considering the mutual action of the atoms of the anisotropic molecules concerned. When the symmetrical elements in the molecule are arranged so that two of their principal planes are parallel, the rotation should be proportional to the square of the birefringence. He considers that in every asymmetric medium there are three directions of propagation of electromagnetic disturbances mutually at right angles, so that the properties of the medium may be completely specified by two symmetrical tensors, the electro-elastic tensor which determines the refractive index, and the rotatory tensor which determines the optical activity.

W. Pfleiderer [29] has measured the absorption spectra, the refractive dispersion, and the optical and magnetic rotatory dispersions of some coloured derivatives of camphor and finds that all the dispersions are anomalous. He has also shown that the magnetic rotatory power of toluene in the visible region of the spectrum is proportional to $\lambda dn/d\lambda$. The magnetic rotatory dispersions of water and ethyl alcohol [30] and of methyl and *n*-propyl alcohols [31] have been measured for a considerable distance into the ultra-violet region of the spectrum, and in all cases the results can be expressed by equations of the form $n\delta\lambda^2 = K[\lambda^2/(\lambda^2 - \lambda_0^2)]^2$, where n is the refractive index at wave-length λ, δ is Verdet's constant, λ_0 is the wave-length of the absorption band controlling the dispersion, and K is a constant. The values of λ_0 for water and for methyl, ethyl, and *n*-propyl alcohols are found to be 0·1192, 0·1100, 0·1114, and 0·1138 μ, respectively, and it is satisfactory to observe that these are the octave harmonics of weak bands actually observed (in the case of the alcohols) at 0·2207, 0·2231, and 0·2273 μ, respectively. It is considered that the vibrations of lower frequency corresponding to these latter bands do not contribute materially to the magnetic rotatory power. It is somewhat remarkable that the magnetic rotatory powers of mixtures of water and ethyl alcohol cannot be calculated from a linear-mixture law, since the curve obtained when the compositions of such mixtures are plotted against their Verdet's constants is markedly sigmoid in character. G. Calcagni[32] has investigated the action of a magnetic field on optically active as well as on optically inactive substances. He finds that for all substances, whatever their concentration, a **S**-pole at the observer end of the tube gives rise to *l*-rotation.

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[24] E. Darmois and R. Descamps, *Compt. rend.*, 1927, **185**, 705; **A.**, 1927, 1126; see also T. S. Patterson and C. Buchanan, *J.*, 1928, 3006.

[25] R. Descamps, *Compt. rend.*, 1927, **184**, 1546; **185**, 116; **A.**, 1927, 723, 823.

[26] E. Darmois, *ibid.*, **184**, 1239, 1438; **A.**, 1927, 610, 723; *Ann. Physique* 1928, [x], **10**, 70; **A.**, 1320.

[27] *Compt. rend.*, 1928, **186**, 857; **A.**, 461; see also P. C. Austin, *J.*, 1928, 1825, 1831.

[28] *Compt. rend.*, 1927, **184**, 1241, 1374; **A.**, 1927, 610.

[29] *Z. Physik*, 1926, **39**, 663; **A.**, 1927, 8.

[30] D. J. Stephens and E. J. Evans, *Phil. Mag.*, 1927, [vii], **3**, 546.

[31] D. O. Jones and E. J. Evans, *ibid.*, 1928, [vii], **5**, 593; **A.**, 461.

S. Mitchell[32a] has added one more to the very small number of substances which have been shown to exhibit the Cotton effect (a maximum of rotatory power on one side of an absorption band and a minimum on the other). Caryophyllene nitrosite forms a blue solution in alcohol, and its rotatory dispersion curve in this solvent has a positive maximum at $\lambda = 0{\cdot}6250$ μ, passes through zero at $\lambda = 0{\cdot}6800$ μ, and is thereafter negative. Its absorption spectrum shows a narrow band with its head at $\lambda = 0{\cdot}6800$ μ. Further value is added to these observations by the fact that the absorption spectra for this solution for right- and left-handed circularly polarised light were examined, and it was found, in accordance with expectation, that the extinction coefficients for left-handed circularly polarised light were greater than the corresponding values for right-handed circularly polarised light.

The Law of Mass Action.

R. D. Kleeman[33] has questioned the accuracy of the law of mass action in the form $\log K = \Sigma\nu \log p$ deduced by van 't Hoff for reactions between perfect gases. He draws a distinction between molecules which dissociate when isolated from a reaction system and those which do not. He terms the former class "sepro-unstable" and the latter class "sepro-stable," and considers that gaseous reactions in general involve both kinds of molecule. For instance, in the reaction $2CO_2 \rightleftharpoons 2CO + O_2$, since there is a possibility of the further reaction $O_2 \rightleftharpoons 2O$, CO_2 and O_2 are termed sepro-unstable, and CO and O sepro-stable. Sepro-stable molecules obey the gas laws, but sepro-unstable ones do not unless by dissociation they give rise to the same number of resultant molecules as reactant molecules which disappear. In fact, whilst the equation of state for one mole of a sepro-stable ideal gas is $v = RT/p$, that for one mole of a sepro-unstable ideal gas is $v = RT/p + \Sigma(A_n/p_n)$, where A_n is a function of the absolute temperature and ΣA_n is zero for a sepro-unstable gas which does not undergo change of volume on dissociation. By considering a gas reaction $aA + bB \rightleftharpoons cC + dD$, where A and B are sepro-stable and C and D are sepro-unstable, employing the classical method of van 't Hoff's equilibrium box, and applying the perfect-gas law to A and B, but the above modification of it to C and D, he arrives at the result that the equilibrium constant, K, is dependent on a factor $e^{X/KT}$, where X is a function of the partial pressures of the reacting gases and hence of the volumes, temperature, and masses of the components of the mixture. Only when $X = 0$ is van 't Hoff's classical derivation, which ignores the possibility of sepro-instability, valid. In some cases X is small for relatively large degrees of sepro-instability, in which case, of course, the law as here derived is very little different from the classical form. The classical law is also a close approximation to this newer form when the degree of sepro-instability is either very small or very great. The possibility of the dependence of the equilibrium constant on the volumes and masses of the reacting gases may also be deduced from kinetic considerations. In a gas reaction, *e.g.*, $2CO_2 \rightleftharpoons 2CO + O_2$, the chance of dissociation depends on the probability of collision of two molecules of CO_2, *i.e.*, on $k_1[CO_2]^2$, where k_1 is the velocity coefficient, but since only activated CO_2 molecules will react, an activation factor, κ_1, must be introduced, the value of which must depend on the number and kind of previous collisions which the molecule has suffered. We then have

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[32] *Notiz. chim.-ind.*, 1927, **2**, 429; *Chem. Zentr.*, 1927, ii, 2263; **A.**, 1928, 461.

[32a] *J.*, 1928, 3258.

[33] *Phil. Mag.*, 1928, [vii], **5**, 268; **A.**, 239.

$$\text{number of molecules dissociating per second} = \kappa_1 k_1[CO_2]^2.$$

Similarly, for the reverse action,

$$\text{number of molecules recombining per second} = \kappa_2 k_2[CO]^2[O_2].$$

Hence $K = \kappa_1 k_1/\kappa_2 k_2$. Since k_1 and k_2 express chances of encounter per unit concentration and are therefore dependent only on the absolute temperature, but κ_1 and κ_2 depend upon the frequencies of the encounters and upon their nature, and are therefore functions of the temperature, volumes, and masses of the reactants, we see that unless $\kappa_1 = \kappa_2$, K will also be a function of these variables.

In a subsequent paper [34] this author considers a reaction $M_a a + M_e e \rightleftharpoons$ various molecules, and derives a differential equation

$$v(\partial p/\partial v)_{T, M_a, M_e} - M_a v_a(\partial p_a/\partial v)_{T, M_a, M_e} - M_e v_e(\partial p_e/\partial v)_{T, M_a, M_e} = 0$$

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[34] *Phil. Mag.*, **1928**, [vii], **5**, 620; **A.**, 589.

by classical thermodynamic methods, and also a similar one when the mass of one of the reactants is the independent variable instead of the volume. The former equation is applied to various cases of gaseous reacting systems to evaluate the functional dependence of K upon v, T, and M. Special cases for which K is a function of T only are discussed. In this paper the ideal-gas law is employed in the form $pv = MRT$, but in two later papers [35] the same author arrives at the conclusion that the thermodynamically correct equation is $pv = \xi MRT$, where ξ is a function of T which becomes zero when $T = 0$. It is also a function of v but does not differ appreciably from unity unless v is very large. This result has a very far-reaching effect on the kinetic theory of gases, and it is deduced, amongst other results, that gaseous substances which do not interact chemically nevertheless affect each other's internal energies by contact, so that the nature of matter must be continually changing, and an atom must therefore bear the impression of all its previous history. It also follows that the equilibrium constant of the law of mass action is almost always a function of the volumes and masses of the reactants from this cause also, but that this effect is appreciable only when the volume is very large. In continuation of these investigations,[36] the nature of the dependence of ξ on the volume of the system is derived and it is concluded that ξ decreases as v increases. Several applications of this theory are studied and a method of experimental investigation is suggested, but it is pointed out and emphasised that the magnitudes of these effects are very small indeed, and that they may even elude measurement at present. "But temporary changes may be induced in the atoms of a substance which give rise to a temporary and pronounced departure in the chemical behaviour as shown by the phenomenon of catalytic action."

These somewhat startling results have not escaped criticism, and R. F. Goldstein [37] has raised objections to Kleeman's derivation of the law of mass action for sepro-unstable molecules, but gives too few details to enable the value of his objections to be assessed. He also asserts that Kleeman's factor κ in his kinetic derivation is merely the activity coefficient of the concentration term. In his reply,[38] Kleeman derives his original expression in another way and disposes of the second criticism by taking a concrete example. Another reply to Goldstein's second point, although it has not been mentioned by Kleeman, would appear to be that, since the derivation is applied to perfect gases, the activity coefficients are by definition equal to unity, and hence cannot be identified with κ.

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[35] *Phil. Mag.*, 1928, [vii], **5**, 668, 1191; **A.**, 470, 955.

[36] *Ibid.*, 1929, [vii], **7**, 53. [37] *Ibid.*, p. 205. [38] *Ibid.*, p. 206.

Cohesion of Solids.

The problem of the laws of interatomic and intermolecular force was rather neglected in the early part of this century, but present-day demands on engineering materials are rapidly emphasising its importance. In a general survey of the problem of cohesion, C. H. Desch [39] summarises the phenomena of interest to the engineer and metallurgist, depending on the nature of cohesion, under ten heads : (1) the tenacity of solids as measured by ordinary tensile tests is very much less than that demanded by theory; (2) the elastic limit is not a physical constant—permanent deformation, especially in single crystals, appears to set in at the lowest stresses which can be applied; (3) failure under alternating load is by fatigue at lower stresses than those which cause failure under static load; (4) cold working has a remarkable effect on the properties of materials; (5) strain depends on the rate of application of stress; (6) the inter-crystalline boundaries have important effects on the properties of solids; (7) the nature of crystalline surfaces is of importance in the study of lubrication and welding problems; (8) the problem of adhesives and solders and the coherence of electrolytic deposits; (9) the diffusion of solids; and (10) the nature of cohesion and its relation to the intrinsic-pressure term in the gas equation of van der Waals.

A. F. Joffé [40] has investigated the first of these points by means of some ingenious experiments on rock-salt. By simple tensile test, this crystal fails at about 0·4 kg./mm.^{2}, whereas theory predicts a tensile strength of 200 kg./mm.^{2}; by ordinary electrical methods, too, rock-salt fails at about 300,000 volts/cm., whereas theory requires a dielectric strength of about 100,000,000 volts/cm., a discrepancy of almost exactly the same ratio. In the mechanical tests, the results are vitiated by the presence of minute cracks on the surface of the crystal which cause intense localisations of stress, and by rapidly removing these cracks (which take time to develop) by solution, breaking loads much nearer to the theoretical are obtained. In this manner, breaking stresses up to 160 kg./mm.^{2} were observed. The fact that no increase in breaking load was observed when the crystal was immersed in saturated salt solution, which obviously cannot dissolve its surface, is an indication that the above explanation of the effect is the correct one and that the increase in strength was not caused by plastic deformation of the crystal by testing in water. Nevertheless, the possible objection that plastic deformation was responsible for the observed increase in strength was removed by carrying out the experiment in another manner. A sphere of the material was subjected to stresses produced by unequal thermal expansion. It was first cooled in liquid air and then plunged into molten lead. By this means it was subjected to a stress of 70 kg./mm.^{2} and it did not fail under this severe treatment. The discrepancy between the observed and theoretical electrical strengths is due mainly to (*a*) the production of Joule heat in the material, (*b*) ionisation by collision, (*c*) irregular distribution of the field, and (*d*) mechanical stress set up by the field. It has been completely removed in the case of other dielectrics (glass and mica) by using films 0·2 μ in thickness. Further reduction in thickness to 0·014 μ did not cause any increase in dielectric strength. These results open up interesting possibilities in connexion with the preparation of insulators, condensers, etc.

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[39] *Trans. Faraday Soc.*, 1928, **24**, 53; **A.**, 111.

[40] *Ibid.*, p. 65; **A.**, 111; *Physikal. Z.*, 1927, **28**, 911; **A.**, 112.

The plasticity of metals and the behaviour of single crystals have been studied by M. Pólányi [41] and G. Sachs,[42] and it is shown that slip planes and lines are always lattice planes and lines in monocrystalline bodies, and that, in general, the most important planes and lines are those which are most closely packed with atoms. Experiments on fatigue and elastic hysteresis in metals are described by H. J. Gough [43] and B. P. Haigh,[44] and the latter author shows that the hysteresis–time curves obtained when annealed ductile metal rods are subjected to approximately sine-wave tensile stresses at a frequency of 2000 cycles per second are characterised by three well-defined sections : (*a*) a brief evolution of heat over not more than $2·5 \times 10^5$ cycles, during which period the hysteresis falls to a minimum value, (*b*) a nearly constant, but slowly rising value of the hysteresis, and (*c*) a rapid increase of hysteresis, immediately followed by fracture. The properties of non-metallic elements in relation to their cohesive forces have been studied by A. M. Taylor,[45] who points out that cohesion may be explained in terms of attractive forces between electric doublets or between unlike charges. In non-metals, the bonds are homopolar and the cohesion originates in the forces between electric doublets, whilst in polar salts (with heteropolar linkages), the force between the ionic charges is superimposed on this. The electric doublets are produced by the deformation of the electron shells surrounding each nucleus, and have a moment $p = \alpha E$, where E is the intensity of the electric field producing the deformation. The constant α may be obtained from the atomic refractivity or from the correction to the Rydberg constant in the formula for the series spectra of the element. The cohesive force is then given by

$$F_c = \Sigma F_e(r) + \Sigma F_p(r) - \Sigma F_R(r),$$

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[41] *Trans. Faraday Soc.*, 1928, **24**, 72; **A.**, 9. [42] *Ibid.*, p. 84; **A.**, 111.
[43] *Ibid.*, p. 137; **A.**, 111. [44] *Ibid.*, p. 125; **A.**, 111. [45] *Ibid.*, p. 157; **A.**, 111.

in which the first term represents the effect of the ionic charges, the second that of the electric doublets, the third the repulsion of the electron shells, and r is the lattice dimension. In polar lattices, the cohesive forces vary inversely as the square of the distance, provided that no deformation of the electron shells occurs. Since this latter effect gives rise to electric doublets, the force between which varies inversely as the fourth power of the distance, increase in α is accompanied by an increase in the compressibility, and this effect is shown by potassium chloride, bromide, and iodide. For non-metallic elements both α and the compressibility are high, and the force between two doublets may be written $F = Cp^2/r^4 - \beta/r^n$, where C, β, and n are constants. By elimination of β, this leads to $F' = -Cp^2(4 - n)/r^5$, whilst for salts the corresponding expression is $F' = -(er)^2(2 - n)/r^5$. Since p is small compared with er, and $(4 - n)$ for non-metals is smaller than $(2 - n)$ for salts, the high compressibility of non-metallic elements compared with salts is in accordance with theory. F' varies more rapidly with r in non-metallic elements than in polar salts, *i.e.*, the restoring force acting on a displaced particle is more markedly anharmonic in non-metals than in salts. This points to a higher coefficient of thermal expansion in the former case, which is in agreement with observation. The cohesion of soldered joints has been studied by T. B. Crow,[46] who finds that, with electrolytic copper rods joined by eutectic solder, contact alloys were formed at the joins and that fracture occurs through these.

T. W. Richards,[47] after reviewing the progress of research (largely his own) on the relation between the volumes and compressibilities of solids and the comparison of the energy changes with the changes of volume which occur during a chemical reaction, arrived at the conclusion that both cohesion and chemical affinity exert pressure which tends to diminish the volume of the system concerned. The main influences at work in any physico-chemical atomic contacts may be represented by an expression equating compressing and distending agencies in equilibrium, thus, $p + \pi = \pi_\rho + P_\theta$, in which p represents the external pressure, π the sum of all the intrinsic compressing effects, π_ρ the intrinsic repulsive effects, and P_θ the thermal pressure, which may be approximately evaluated as $T\alpha/\beta$, where α and β are the coefficients of thermal expansion and compressibility, respectively. Since both π and π_ρ are observed to diminish with increase of volume, this equation may be written

$$p + \pi_0(v_0/v)^m = {}_0\pi_\rho(v_0/v)^n + T\alpha/\beta$$

where the subscript $_0$ indicates properties measured in some standard state, and m and n are unknown and are not necessarily constant.

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[46] *Trans. Faraday Soc.*, 1928, **24**, 159.

[47] *Ibid.*, p. 111; **A.**, 112.

However, n must certainly be greater than m, otherwise a slight increase of external pressure would cause the substance to collapse. This equation leads to an expression for the internal pressure, $\pi_0 = 1/\beta(n - m)$. The values of π_0 for different elements computed by means of this equation are large, but appear quite reasonable. For binary compounds the equation

$$\beta = \frac{x}{(n - m)}\left(\frac{x}{\pi_1} + \frac{x - 1}{\pi_2}\right)$$

is suggested, in which x is the fraction of each atom subjected only to cohesive pressure, π_1, and $(1 - x)$ is the fraction subjected to intense chemical pressure, π_2. It is estimated that whilst, for example, the pressure between the molecules of liquid bromine is of the order of 5000 atmospheres, that between the bromine atoms in the molecule is of the order of 100,000 atmospheres. From the numerical values of this kind thus deduced, it appears that the widely held view, that the latent heats of vaporisation and of chemical reaction represent simply the net amount of work done by affinity when molecules (in the former case) or atoms (in the latter) approach one another from a considerable distance, is correct.

The value of the index in a power law of molecular force is discussed by A. W. Porter,[48] but it is concluded that no trustworthy deduction can yet be made. Glass is considered as a fourth state of matter[49] since there is a marked discontinuity in the physical properties, *e.g.*, the heat capacity, when a liquid passes into the glassy form. Moreover, the glassy and crystalline states have nearly the same heat capacity. A glass, like a liquid, possesses a random arrangement of its units but, like a solid, is held together by fixed, rigid linkings. It is considered improbable that the glassy layer formed by polishing a solid surface is the result of actual liquefaction, since, once a group of molecules is torn from its position in the lattice, it is practically impossible, under ordinary polishing conditions, to force it back within the range of molecular cohesion,[50] and, moreover, the solidification of a fused layer might result in recrystallisation.[51] The compressibility of metallic alloys has been studied by R. F. Mehl and B. J. Mair,[52] who find that it is always less than that indicated by the simple-mixture law, the deviation increasing as the dissimilarity of the metals increases. The difference is attributed to the chemical affinity of the metals. A classification of metallic substances into the following groups has been suggested [53]: (*a*) metallic elements, which may be isotopically simple or complex; (*b*) primary metallic solid solutions which retain the crystal structure of the parent metal and form the end phases of ordinary equilibrium diagrams; (*c*) secondary solid solutions with a crystal structure different from that of the parent metal, but with no indication of the formation of compounds; and (*d*) intermetallic compounds. W. Hume-Rothery has also critically reviewed existing theories of the metallic state.[54] Drude's electron gas theory, the electrical doublet theory of Thomson, the theory of Wien and Gruneisen, Lindemann's electron lattice theory, and Bridgman's theory all account more or less for the electrical and thermal properties of metals, but Lindemann's theory is the only one which is in general agreement with compressibility data and tensile properties. It is also the only one which gives an explanation of the plasticity of metals, which is considered to be due to the relatively great size of the positive ions compared with the electrons which form the other components of the lattice. The supraconductivity shown by some metals at the temperature of liquid helium is considered to be due to the precessional motion of the elliptic electronic orbits causing the zones of repulsion round the metallic ions to vary periodically. This conception agrees with the fact that supra-conductivity is shown by some metals and not by others. New statistical methods have been applied to the problem of the distribution of electrons in a metal by J. E. Lennard-Jones and H. J. Woods,[55] by A. Sommerfeld [56] to account for electrical and thermal effects, and by other workers in studies of electron emission from cold metals [57] and of the Volta effect.[58]

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[48] *Trans. Faraday Soc.*, 1928, **24**, 108.

[49] G. S. Parks and H. M. Huffman, *Science*, 1926, **64**, 363; **A.**, 1927, 300.

[50] J. W. French, *Nature*, 1927, **119**, 527; **A.**, 1927, 510.

[51] N. K. Adam, *ibid.*, p. 162; **A.**, 1927, 192.

[52] *J. Amer. Chem. Soc.*, 1928, **50**, 55; **A.**, 229; see also R. F. Mehl, *Amer. Inst. Min. Met. Eng.*, Tech. Pub., 1928, No. 57; **A.**, 699.

Oxide Films on Metals.

The study of metallic corrosion has greatly extended our knowledge of the properties and the conditions of formation of oxide films upon the surface of metals. It will be convenient to discuss this subject under two headings: (*a*) films formed by atmospheric action, and (*b*) films formed by electrolytic action.

(a) *Films formed by Atmospheric Action.*—The production of colours (temper colours) on steel and other metals has generally been assumed to be due to the formation of transparent oxide films which are sufficiently thin to give rise to interference effects.[59] This has been confirmed experimentally by U. R. Evans,[60] who has shown that the bands of colour produced by heating one end of a strip of iron can be caused to move along the strip without changing their order if the thickness of the graduated film of oxide is uniformly diminished by careful cathodic reduction in dilute acid. A similar effect has been obtained by C. W. Mason [61] by simple solution in acid, and by R. C. Gale [62] by polishing. Confirmatory evidence of the real existence of an oxide film on passive iron mirrors deposited on glass by thermal decomposition of the pentacarbonyl has been obtained [63] by following the changes in the condition of polarisation of the light reflected from the mirrors before and after exposure to the air. F. H. Constable [64] has shown that oxidation colours on copper may be made homogeneous if precautions are taken in preparing the film to ensure uniform oxidation at all parts of the surface. His results agree with the interference theory, and the absolute thickness of the oxide film calculated from the density of the oxide and the mass of oxygen absorbed per unit area of surface agrees moderately well with the thickness calculated from the position of the absorption band and the corresponding refractive index. The connexion between tarnishing and reflecting power has also been studied by G. Ando.[65] By means of *X*-ray powder photographs, R. M. Bozorth [66] has found that the protective coating due to the action of steam on iron at 700°, followed by cooling in air, consists of layers of FeO, Fe_3O_4, and Fe_2O_3 in the order of oxidation, the respective thicknesses being estimated as 100, 2, and 0·2 μ. The rate of formation of oxide films on metals has been studied very thoroughly by using optical, electrical conductivity, and gravimetric methods. N. B. Pilling and R. E. Bedworth [67] find that at high temperatures copper, nickel, zinc, and iron obey a parabolic law, $W^2 = kt$, for the increase of weight with time. Cadmium and aluminium show a similar behaviour at first, but the rate of increase of weight diminishes rapidly later. J. S. Dunn[68] finds a similar law for 95/5 and 90/10 brass, but suggests $W^n = k_1t$ for 71/29 brass, where n is slightly greater than 2. In a later paper,[69] he finds that between 209° and 284° copper obeys the parabolic law, but that about 200° deviations occur which he attributes to the existence of a transition point for the oxide near this temperature.

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[53] W. Hume-Rothery, *Phil. Mag.*, 1928, [vii], **5**, 173; **A.**, 222.

[54] *Idem, ibid.*, 1927, [vii], **4**, 1017; **A.**, 111.

[55] *Proc. Roy. Soc.*, 1928, [*A*], **120**, 727; **A.**, 1299.

[56] *Z. Physik*, 1928, **47**, 1, 43; **A.**, 467; see also *Naturwiss.*, 1927, **15**, 825; 1928, **16**, 374; **A.**, 681.

[57] W. V. Houston, *Z. Physik*, 1928, **47**, 33; **A.**, 467.

[58] C. Eckart, *ibid.*, p. 38; **A.**, 467.

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[59] G. Tammann, *Z. anorg. Chem.*, 1920, **111**, 78; 1922, **124**, 25; G. Tammann and W. Köster, *ibid.*, 1922, **123**, 196; *A.*, 1922, ii, 831.

[60] *Proc. Roy. Soc.*, 1925, [*A*], **107**, 228; *A.*, 1925, ii, 288.

[61] *J. Physical Chem.*, 1924, **28**, 1233; *A.*, 1925, ii, 108.

[62] *J. Soc. Chem. Ind.*, 1924, **43**, 349T; *A.*, 1925, ii, 109.

[63] H. Freundlich, G. Patscheke, and H. Zocher, *Z. physikal. Chem.*, 1927, **128**, 321; **130**, 289; **A.**, 1927, 1037, 1149.

[64] *Proc. Roy. Soc.*, 1927, [*A*], **115**, 570; **A.**, 1927, 930.

[65] *Mem. Coll. Sci. Kyoto*, 1928, [*A*], **11**, 85; **A.**, 717.

[66] *J. Amer. Chem. Soc.*, 1927, **49**, 969; **A.**, 1927, 502.

[67] *J. Inst. Metals*, **1923, 29,** 529.

W. H. J. Vernon[70] finds that heating copper for a short time in air at 75° confers immunity from tarnishing, presumably by the formation of an invisible oxide film. The fact that similar heating at 55° does not have this effect suggests that there is a minimum thickness of the film required for protection, and calculation indicates that this minimum film is the unit lattice of cuprous oxide. In the "Second Experimental Report to the Atmospheric Corrosion Research Committee (British Non-Ferrous Metals Research Association),"[71] this author distinguishes three kinds of weight increment–time curve at ordinary temperatures :

(i) The parabolic relationship already referred to, where the process of tarnishing is regulated by the diffusion of the atmosphere through a continuous solid film which itself thickens as a result of this process. This is true for copper except at the very beginning of the process when the film is not completely formed (on a plate of metal the film forms from the edges, inwards). In this case, it is somewhat remarkable to note that the rate of attack is determined by the conditions prevailing at the time of the initial exposure, and that the external conditions may subsequently vary within extremely wide limits without disturbing the course of the attack. He also finds that oxide films on copper are relatively impervious to oxygen at ordinary temperatures, and very impervious to hydrogen sulphide, but that sulphide films are relatively pervious to both oxygen and hydrogen sulphide.

(ii) A linear relation, $W = k't$. This is the case with a pervious film like that on zinc, where the velocity of oxygen addition depends only on the rate of diffusion of the atmosphere to the surface to be attacked.

(iii) A curve beginning as a parabola and rapidly flattening towards the time axis. This kind of curve is obtained with aluminium and lead. It is characteristic of the adsorption isotherm, and it is suggested that this phenomenon plays a part in the mechanism of formation of the film. The curves obtained for brass in their earlier stages resemble the copper curves, but in their later stages resemble those for zinc.

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[68] *Proc. Roy. Soc.*, 1926, [*A*], **111**, 203. [69] *Ibid.*, p. 210. [70] *J.*, 1926, 2273.
[71] *Trans. Faraday Soc.*, 1927, **23**, 113; **B.**, 1927, 526.

The variation of the velocity of film formation with temperature has also been studied in the case of copper,[68, 70, 72] and has been found to follow the van 't Hoff isochore. The slope of the straight line obtained when the logarithm of the velocity coefficient is plotted against the reciprocal of the absolute temperature is less for film formation than in the case of the similar curve for the dissociation of cupric oxide, thus indicating that the intermediate formation of this oxide is not a possible mechanism. An empirical equation, $K = aT^{\theta}$, has also been proposed for the variation of K, the oxidation velocity coefficient, with temperature for copper [67] and for 60/40 brass.[70]

(b) *Films formed by Electrolytic Action.*—Temper colours have been produced by anodic attack on iron in aqueous caustic soda by superimposing alternating on the direct current,[72] and also by the action of chromate solutions containing chloride.[73] The oxide-film theory of passivity, however, has not hitherto secured full acceptance, chiefly for two reasons : (i) no film is usually visible on a passive metal, and (ii) metals covered with a visible film are often not passive. The second objection may be met by pointing out that a film which is thick enough to be seen is likely to crack because of the difference between the specific volumes of the oxide and that of the metal contained in it.[67] The first objection has now been removed by U. R. Evans,[74] who has isolated the film of oxide which causes passivity of iron. Pure electrolytic iron was rendered passive by treatment with chromate, nitrite, or caustic soda, and the film was ruptured along a line, either by trimming the metal or by scratching. The iron was then removed by anodic treatment in sodium chloride solution or by dissolving it in a saturated solution of iodine in potassium iodide. In this manner the film was obtained as thin transparent flakes preserving the original form of the surface of the specimen. This film is permeable to chloride ions, which may therefore cause the underlying iron to be attacked if conditions are such as to allow of the production of local electric currents. Similar films were isolated from passive copper and aluminium, but the passivity of copper is less persistent than that of iron, although the passivity of aluminium is more so. No film could be isolated from iron passivated in nitric acid, but E. S. Hedges [75] has obtained convincing indirect evidence of its existence and nature. He has shown that the lowest concentration of nitric acid required to passivate electrolytic iron at 30° is 86%, and that this result is reproduced with ease, provided that great care is taken to ensure that the specimen is passed rapidly through the surface of the acid, which has an activating effect. By whirling passive iron at 3000 r.p.m. in concentrated nitric acid, it becomes active after a short period of induction which corresponds to the time taken to dissolve the film of oxide. This result is counter to the theory of A. Smits,[76] which predicts that the more rapid removal of ions from the surface of the metal by whirling should produce a greater disturbance of the inner equilibrium at the surface, and should thus produce a greater passivity. The reality of the presence of the oxide film on the surface of passive iron is shown by the fact that this metal begins to dissolve in nitric acid at 74·5—75·5° whatever the concentration of the acid, and that freshly ignited ferric oxide is not appreciably dissolved by concentrated nitric acid until this temperature is reached. Other metals (cobalt, nickel, and copper) are rendered passive by concentrated nitric acid at -11°. The fact that passivity is shown by metals outside the iron group indicates that explanations based on the theory that passivity is due to the assumption by the metal atoms of an electron structure of the inert-gas type (*e.g.*, for iron, 2, 8, 8, 8 instead of 2, 8, 14, 2), as suggested by A. S. Russell,[77] S. Glasstone,[78] and W. D. Lansing,[79] are not likely to be correct. Hedges has also shown that anodic films—not necessarily of oxide—are formed, in some cases in a periodic manner, by copper and silver,[80] zinc, cadmium, mercury, tin, and lead,[81] and iron, cobalt, nickel, and aluminium,[82] and that these films follow the regions of high current density at the edges and corners of a rectangular electrode.[83] G. Grube [84] has reviewed and discussed some theories of passivity, and concludes that anodic passivity is caused in iron, cobalt, and manganese by the deposition of films of oxide of the type M_3O_4.

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[72] A. J. Allmand and R. H. Barklie, *Trans. Faraday Soc.*, 1926, **22**, 34; **B.**, 1926, 277, 497.

[73] U. R. Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163T.

[74] *J.*, 1927, 1020.

[75] *Ibid.*, 1928, p. 969.

Electrode Potentials.

The use of oxidation–reduction potentials in biological work is rapidly extending, and an adequate introduction to the theory and practice of the various methods employed is to be found in W. M. Clark's " The Determination of Hydrogen Ions," which has now attained a third edition.[85] The treatment of the subject by means of a space model with p_H, percentage oxidation, and potential as co-ordinates brings out well the dependence of oxidising or reducing intensity on p_H, and the method is capable of wider application. The use of the symbol r_H to denote the decadic logarithm of the reciprocal of the equivalent hydrogen pressure of an oxidation–

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[76] " Theory of Allotropy," Longmans, 1922, p. 345.

[77] *Nature*, 1925, **115**, 455; 1926, **117**, 47; *A.*, 1925, ii, 406; **A.**, 1926, 133.

[78] *J.*, 1926, 2887.

[79] *Physical Rev.*, 1927, [ii], **29**, 216; **A.**, 1928, 1303.

[80] *J.*, 1926, 1533.

[81] *Ibid.*, p. 2582.

[82] *Ibid.*, p. 2878.

[83] *Ibid.*, 1927, 2710.

[84] *Z. Elektrochem.*, 1927, **33**, 389; **A.**, 1927, 1034.

[85] Baillière, Tindall and Cox, 1928.

reduction system is now discouraged by its originator [86]—it has evidently proved a dangerous tool in unskilled hands. The number of oxidation–reduction indicators continues to increase. A colorimetric method of determining oxidation–reduction potentials has been worked out for methylene-blue by P. Hirsch and R. Rüter.[87] This is somewhat similar to the well-known method for p_H, but since another variable, the acidity of the solution, affects the results, it is necessarily somewhat more complicated. M. Phillips, W. M. Clark, and B. Cohen [88] have made potentiometric and spectrophotometric studies of Bindschedler's green and toluylene-blue for this purpose, and have compared the behaviour of the indamine dyes with that of the thiazines—the basic indamine dyes form useful alternative oxidation–reduction indicators to the acidic indophenols. E. Aubel, L. Genevois, and R. Wurmser [89] have determined the oxidation–reduction potentials of a number of dyes, and G. Blix [90] has investigated the decolorisation time of methylene-blue in hexose-phosphate mixtures. Oxidation–reduction buffer solutions are also described [87] for various ranges of p_H—for example, cuprous–cupric chlorides in potassium chloride, ferrous–ferric oxalates in oxalate and in citrate buffers. The behaviour of various dyes in accelerating the attainment of oxidation–reduction potentials in systems containing dextrose has also been studied.[91]

The polarographic method of determining oxidation–reduction potentials of organic compounds at a dropping-mercury cathode by the automatic tracing of voltage–current curves has been described.[92] It has been applied to *iso*valeraldehyde,[93] for which the equation $\pi = -RT/2F \, . \log k'/\{[H^+]^2 \times C^{1/m}_{R\cdot CHO}\}$ is valid. For a $0{\cdot}1868M$-solution in $0{\cdot}1N$-hydrochloric acid, $\log k' = 34{\cdot}672$, and m—the adsorption coefficient for the aldehyde at the electrode—is 1·380 in a strongly acid solution, and depends on the p_H of the solution. It is claimed that the polarographic method is twenty times as sensitive as Schiff's reagent for the detection of aldehydes. When this method is applied to the reduction of pyridine solutions,[94] the agreement between the observed results and the equation is less satisfactory, especially in alkaline solution, but the curves obtained indicate that reduction of both ions and molecules of pyridine occurs. The reduction of nicotinic acid [95] by this method occurs

[86] *Op. cit.*, p. 387. [87] *Z. anal. Chem.*, 1926, **69**, 193; **A.**, 1927, 23.

[88] *U.S. Public Health Service*, Suppl. 61; **A.**, 129.

[89] *Compt. rend.*, 1927, **184**, 407; **A.**, 1927, 316.

[90] *Skand. Arch. Physiol.*, 1927, **50**, 8; *Chem. Zentr.*, 1927, ii, 1352; **A.**, 1928, 250.

[91] R. Wurmser and J. Geloso, *Compt. rend.*, 1928, **186**, 1842; **A.**, 846.

[92] M. Shikata, *Mem. Coll. Agric. Kyoto*, 1927, **4**, 1; **A.**, 1928, 136.

[93] M. Shikata and I. Tachi, *ibid.*, p. 9; **A.**, 1928, 136.

[94] *Idem, ibid.*, p. 19; **A.**, 1928, 136. [95] *Idem, ibid.*, p. 35; **A.**, 1928, 136.

in two stages. The method has also been applied to the micro-detection of lead and copper,[96] and of reducing substances in fermented liquors.[97] It has been shown by the same method that the normal reduction potentials of maleic and fumaric acids are identical.[98]

A study of Haber's glass electrode has been made by W. S. Hughes,[99] and it is recommended that the glass used should be as free as possible from potash, alumina, and borates : the bulb should be thin and devitrification should be avoided. The behaviour of the cell is best explained on the hypothesis that the hydrogen-ion concentration in the glass phase is maintained relatively constant by the buffer action of the sodium acid silicate contained in it. Many metals are capable of utilisation as electrodes to give end-points in the potentiometric titration of acids and bases, and successful results by using tungsten, molybdenum, arsenic, antimony, bismuth, aluminium, and tin for this purpose have been recorded.[1] The antimony–antimony trioxide electrode [2] has been very fully investigated, and it is considered that the unsatisfactory results hitherto obtained with it are due to the dimorphism of the oxide. Antimony trioxide changes from the cubic to the rhombic form at 570° ± 10°, and the form produced by the hydrolysis of the trichloride is naturally the metastable one (rhombic). Trustworthy results with this electrode are obtained only when this metastable phase and dissolved oxygen are eliminated and equilibrium is approached from the alkaline side. When these precautions are taken, the potential is a linear function of the p_{H}, and the normal potential referred to the hydrogen standard is $+ 0{\cdot}1445 \pm 0{\cdot}002$ volt. Since the electrode thus prepared is permanent and constant and requires little attention, it is considered to be superior to the hydrogen electrode. A new method of avoiding liquid junction potentials, with their attendant uncertainties, in the determination of electrode potentials, has been described.[3] A fine-meshed earthed metal gauze is placed above and parallel to the surface of the solution, and is surmounted by a parallel metal plate connected to an electrometer. The air in the vicinity of the metal gauze is ionised by means of a constant radioactive source, and the potential difference between the electrode and the solution is determined from the changes in the leakage current from the charged electrometer when the electrode, plus a source of known potential in series with it, is connected to earth.

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[96] M. Shikata, *Mem. Coll. Agric. Kyōtō*, p. 49; **A.**, 1928, 136.

[97] M. Shikata and K. Shoji, *ibid.*, p. 75; **A.**, 1928, 136.

[98] P. Herasymenko and Z. Tyvońuk, *Z. Elektrochem.*, 1928, **34**, 74; **A.**, 482.

[99] *J.*, 1928, 491.

[1] J. O. Kloss and L. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, Sept. 1928; **A.**, 1203.

[2] E. J. Roberts and F. Fenwick, *J. Amer. Chem. Soc.*, 1928, **50**, 2125; **A.**, 1098.

[3] M. Andauer, *Z. physikal. Chem.*, 1927, **125**, 135; **A.**, 1927, 316.

A number of new methods of potentiometric titration have appeared. A useful collection of the methods in use up to 1926 has been published,[4] but readers should beware of the mathematical treatment of the titration error on p. 79 which has apparently been competently deduced but has subsequently been badly muddled and unintelligently abbreviated. B. Cavanagh[5] has described an absolute method of potentiometric titration which avoids the use of liquid junctions. It depends on the fact that the *E.M.F.* between two different electrodes in the same solution is $E = E_0 + RT/F \cdot \log (C_1 \times C_2)$, where C_1 and C_2 are the concentrations of the respective ions. The end-point *E.M.F.* for one ion can therefore be calculated if the concentration of the other and the appropriate ionic or solubility products are known. In effect, the method thus consists of combining the reference half-cell in the same solution as that to be titrated. The use of a potentiometer may be avoided by employing an end-point cell of similar construction connected in opposition in the usual manner. Theoretically, it should be possible to adjust the concentration of one ion so that when the other is at the end-point concentration, the total *E.M.F.* is zero, and thus avoid even the use of a reference end-point cell. The possibility of actually realising such conditions, however, depends on the numerical values of the normal electrode potentials concerned. Thus, for example, with a hydrogen and a silver chloride electrode, for the *E.M.F.* to vanish when the $p_H = 7$ would require a chloride-ion concentration of about $10^{11}N$, whereas with a quinhydrone and a silver chloride electrode the corresponding concentration is only $N/450$. Several cases are examined and limits of accuracy are discussed. The same author[6] has devised a modified method of potentiometric titration depending on changes of potential at the indicator electrode, and has given tables from which the end-point of a titration can be evaluated by a method of successive approximation without actually reaching it. The absolute uncertainty of this method is of the order of one-fifth of the solubility of the precipitated salt (or other corresponding constant), but somewhat higher precision may be obtained by modified methods[7]—for which tables and curves are also given—provided that the titration curve conforms to an equation deduced by thermodynamic methods:

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[4] I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," Wiley and Sons, 1926.

[5] *J.*, 1927, 2207.

[6] *Ibid.*, 1928, 843.

[7] *Ibid.*, p. 855.

$$\frac{Mn\sqrt{\gamma\gamma'\theta\theta'}}{2s(V_e - M)} = \sinh\left[\frac{F}{RT}(E - E_e) + \frac{1}{2}\log\frac{\gamma'\gamma_e}{\gamma\gamma'_e} + \frac{1}{2}\log\frac{\theta'\theta_e}{\theta\theta'_e} \pm \log\frac{s}{s_e}\right]$$

In this equation, M denotes the number of c.c. of reagent still to be added to complete the titration, n is the normality of the reagent, γ' and γ are respectively the activity coefficients of the positive and negative ions, θ' and θ are the fractions of the ions not adsorbed by the precipitate, s^2 is the activity product of the ions concerned, V is the volume of the solution, E is the potential of the electrode, F, R, and T have their usual thermodynamic significance, the suffix e denotes end-point values, and the alternative signs in the last term are used in conformity with the sign of the charge on the ion corresponding to the nature of the electrode used. E. Müller and H. Kogert [8] have described a modification of the bimetallic electrode method of potentiometric titration, using electrodes of the same metal and obtaining the end-point by determining the maximum potential difference instead of the maximum rate of change. They have also described a method [9] by which two similar electrodes are placed at some distance apart in the solution to be titrated, the reagent is introduced near one, and the solution is stirred towards the other. The first electrode is therefore in contact with a solution containing excess of the added reagent, and thus acquires a potential different from that of the second, which is in contact with the mixed solution. At the end point, the temporary deflexion of a galvanometer connected across the two electrodes is said to be practically zero.

HAROLD HUNTER.

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[8] *Z. physikal. Chem.*, 1928, **136**, 437; **A.**, 1203.

[9] *Ibid.*, p. 446.

INORGANIC CHEMISTRY.

THE steady revival of interest in Inorganic Chemistry which has been apparent for some years has become more marked during the period covered by this Report. A considerable increase in the volume of useful and interesting work has enhanced the difficulty of selection and adequate treatment. The Report follows the general lines of those of previous years, and the remarks prefacing the Report for 1925, to which the reader's attention may be directed, are applicable in the present case.

Subjects which appear to be of special interest are: helides (p. 40); the chemical evidence that cæsium and titanium are not "simple" elements (pp. 37, 38); the evidence that the heavier isotope of potassium is probably responsible for the radioactivity of that element (p. 42); reactions of beryllium and its salts in liquid ammonia (p. 44); a full investigation of calcium nitrides (p. 45); a new classification of the rare earths (p. 48); the products of the reaction of carbon disulphide with sodium amalgam (p. 50); silicic acids and the silicates (p. 51); germanium compounds (p. 53); nitrogen trifluoride (p. 54); compounds of sulphur and selenium (pp. 57, 58); the chemical properties of rhenium (p. 60).

Reference may be made to a type of glass-to-glass joint on the ball-and-socket principle which appears to have been in use among metallurgists in Germany for some time and to have given excellent results. The pieces of glass forming the joints are flanged and ground to an accurately standardised curvature in the form of balls and sockets which are thus interchangeable. The joints are made gas-tight by the thinnest possible film of grease applied to the engaging surfaces, which are held together by a special clamp. Advantages of such joints are that they may be made between different materials with much less risk of fracture than is the case with ordinary ground joints, that they are flexible to a certain degree, that they do not seize, and that they are made and broken with a minimum of movement of the rest of the apparatus.[1]

Atomic Weights.

Neon and Argon.—The normal density of neon, after exhaustive chemical purification followed by fractional adsorption, is found to be 0·89990, whence the atomic weight is Ne = 20·182. By similar methods the normal density of argon has been found to be 1·78364, whence A = 39·943. By rejecting the conventional assumption that the value of PV for one atmosphere is correct, distributing the errors by finding the best straight line representing the observed values of some simple function of the density plotted against the pressure, and then extrapolating to zero pressure, small differences have been found between the calculated and observed values of the densities at different pressures. The effect on the deduced atomic weight is always less than 0·001 unit, although fortuitously the third decimal place is affected in the case of neon and argon. The values calculated by this method are: Oxygen 16·000, nitrogen 14·008, neon 20·183, argon 39·944. The value of the limiting density of oxygen is 1·42764, which yields as the limiting value of the molal volume 22·4146 litres (g = 980·616).[2]

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[1] E. I. Lewis, *J. Soc. Chem. Ind.*, 1928, **47**, 1238.

Cæsium.—On account of the discordance between the data obtained for this element by chemical methods and by the mass-spectrograph, the ratio CsCl : Ag has been redetermined, the cæsium being purified by recrystallisation of the alums and not, as previously, of the dichloroiodide. Four determinations gave in mean Cs = 132·809 ± 0·012, this "probable" error being within the experimental error, ± 0·015, estimated from the known errors of weighing and titration.[3] This result confirms the accepted atomic weight,[4] Cs = 132·81, and thus indicates a "packing fraction" of -14×10^{-4}, appreciably greater than that to be inferred from Aston's curve.[5] It is therefore suggested (compare titanium, below) that cæsium may be not a "simple" element, as has been supposed, but a mixture of isotopes.

Silver.—A preliminary account of determinations of the ratios $Ba(ClO_4)_2 : BaCl_2 : 2Ag$ indicates that the derived ratio Ag : 4O gives Ag = 107·880, in agreement with the accepted value.[6]

Erbium.—Erbium giving a constant equivalent is obtained from erbium–yttrium material from gadolinite, by fractionation using the nitrate fusion method or by fractional precipitation with sodium nitrite.[7] The mean of six determinations of the ratio $ErCl_3 : 3Ag$

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[2] G. P. Baxter and H. W. Starkweather, *Proc. Nat. Acad. Sci.*, 1928, **14**, 50, 57; **A.**, 343.

[3] T. W. Richards and M. Françon, *J. Amer. Chem. Soc.*, 1928, **50**, 2162; **A.**, 1069.

[4] T. W. Richards and E. H. Archibald, *Proc. Amer. Acad. Arts Sci.*, 1903, **38**, 443; *A.*, 1903, ii, 366.

[5] F. W. Aston, *Proc. Roy. Soc.*, 1927, [*A*], **115**, 487; **A.**, 1927, 914.

[6] O. Hönigschmid, *Z. Elektrochem.*, 1928, **34**, 625; **A.**, 1168.

[7] A. E. Boss (with B. S. Hopkins), *J. Amer. Chem. Soc.*, 1928, **50**, 298; **A.**, 343.

gave Er = 167·64 (Ag = 107·88), a figure but slightly lower than the accepted value 167·68.[8]

Titanium.—Titanium tetrabromide has been purified and analysed by the methods previously employed[9] for the preparation and analysis of titanium tetrachloride which had given Ti = 47·90. Ten determinations[10] of the ratio $TiBr_4 : 4Ag$ have given Ti = 47·900 ± 0·0013, the extreme deviation being for the whole series 0·019 unit and for six of the results less than 0·007 unit. This value confirms the earlier determination and accords with the general rule that the masses of individual isotopes fall short of the integral values when the mass number is between 20 and 200, but it leads to a packing fraction nearly three times as large as that derived from Aston's curve.[5] In the first examination of titanium in the mass-spectrograph, Aston[11] found doubtful indications of an isotope of mass 50, besides the main isotope of mass 48, and it seems possible that the discrepancy may be due to an undiscovered lighter isotope.

Nitrogen.—The mean density of nitrogen, obtained from four different sources, has been found to be 1·25049 ± 0·00003 g./litre. The most probable value of the atomic weight is 14·0082 ± 0·00042.[12]

Antimony.—The ratio $SbBr_3 : 3AgBr$ has been found in 25 determinations[13] on material from five different sources. The results in terms of atomic weight range from 121·744 to 121·754, the variation being less than the estimated experimental error.

Uranium.—Uranous chloride has been prepared and analysed by the methods previously used for the bromide,[14] and 19 determinations of the ratio $UCl_4 : 4Ag$ and 18 of $UCl_4 : 4AgCl$ have been made. The results for both ratios lead to the value U = 238·14.[15]

Intensive Drying.

The work published in this field during the year presents a conflict of evidence and is therefore reported here without comment.

It has been pointed out that the view[16] that the rise in boiling points of substances dried over phosphoric oxide may be due to the presence of phosphoric acid or its esters is untenable, and that the presence of phosphorus in dried liquids is due to phosphorus trioxide in the pentoxide used.[17] Other workers [18] report that, after about 4 years' intensive drying with phosphorus pentoxide at the ordinary temperature, no abnormal rise was observed in the boiling points of benzene and carbon tetrachloride.

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[8] K. A. Hofmann, *Ber.*, 1910, **43**, 2631; *A.*, 1910, ii, 1073.

[9] G. P. Baxter and G. J. Fertig, *J. Amer. Chem. Soc.*, 1923, **45**, 1228; *A.*, 1923, ii, 498; G. P. Baxter and A. Q. Butler, *ibid.*, 1926, **48**, 3117; **A.**, 1927, 86.

[10] *Idem, ibid.*, 1928, **50**, 408; **A.**, 343.

[11] F. W. Aston, *Phil. Mag.*, 1924, [vi], **47**, 397; *A.*, 1924, ii, 225; compare *Ann. Reports*, 1924, **21**, 238.

[12] E. Moles and J. M. Clavera, *Z. anorg. Chem.*, 1927, **167**, 49; **A.**, 1927, 1120.

[13] K. R. Krishnaswami, *J.*, 1927, 2534; **A.**, 1927, 1120.

[14] O. Hönigschmid, *Z. Elektrochem.*, 1914, **20**, 452; *A.*, 1914, ii, 662; O. Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1916, **37**, 185; *A.*, 1916, ii, 484.

[15] O. Hönigschmid and W. E. Schilz, *Z. anorg. Chem.*, 1928, **170**, 145; **A.**, 569.

[16] D. Balarev, *J. pr. Chem.*, 1927, ii, **116**, 57; **A.**, 1927, 613.

Nitrogen peroxide and phosphoric oxide when heated together give rise to at least three simultaneous reactions : (*a*) they form an additive compound ; (*b*) the peroxide is dissociated into nitric oxide and oxygen to a greater extent than is the moist gas, and these products do not recombine in cooling ; (*c*) the nitric oxide decomposes into its elements at a greater rate than normally. The last effect is ascribed to the catalytic effect of the large surface of phosphoric oxide, whilst the relative extent to which these reactions proceed depends on the temperature and duration of the heating. Nitrogen peroxide which has been intensively dried at the ordinary temperature, however, does not dissociate very considerably into nitric oxide and oxygen when heated at 550° for 24 hours, but when heated at 620° for some time seems to revert to the normal state, possibly owing to a superficial decomposition of the glass. In the dried gas the rate of polymerisation of the coloured NO_2 molecules to form colourless N_2O_4 molecules is retarded.[19]

It has been suggested [20] that inner transformations in the liquid phase of a single substance have not yet been stopped by the process of intensive drying, the evidence of surface tension being rejected as an untrustworthy criterion for internal equilibria, and other evidence being discarded on the grounds that it was obtained under conditions of rapid evaporation or distillation which did not allow the attainment of equilibrium.

Group 0.

The observations that the heat of vaporisation of liquid helium shows a maximum near 3° Abs.[21] and that the plot of surface tension against temperature shows a change in direction at 2·4° Abs.[22] have an added significance by reason of the discovery that the heating and cooling curves, taken at 38 mm. pressure, show a slight halt at 2·3° Abs. These data are held [23] to indicate that helium forms two different liquid phases, having a heat of transformation (calculated from the specific heats [24]) of −0·13 g.-cal./g., to yield the form stable at higher temperatures, which has the higher density and surface tension and the lower heat of vaporisation. Similar properties have previously been observed only in more complex substances.

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[17] H. B. Baker, *J.*, 1927, 2902 ; **A.**, 1928, 10 ; *idem, J. pr. Chem.*, 1928, ii, **118**, 96 ; **A.**, 354.

[18] S. Lenher and F. Daniels, *Proc. Nat. Acad. Sci.*, 1928, **14**, 606 ; **A.**, 1189.

[19] J. W. Smith, *J.*, 1928, 1886 ; **A.**, 953.

[20] A. Smits, *J.*, 1928, 2399 ; **A.**, 1189.

[21] L. I. Dana and H. K. Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1051 ; **A.**, 1927, 101.

[22] *Ann. Reports*, 1926, **23**, 52.

Mercury oscillating with the production of a glow discharge in contact with certain pure common gases at pressures of a few mm. has been shown to yield solid compounds, whilst a single experiment with helium resulted in a lessened gas pressure from which the synthesis of a helide was inferred. The first quantitative work led to the formula $HgHe_{10}$, but from one of a series of subsequent experiments, where the pressure changes were almost negligible, the formula HgHe or $HgHe_2$ was deduced from the density of the gaseous mixture, measured with an Aston microbalance, and the weight of mercury obtained by decomposing the compound on a heated platinum spiral and weighing the resultant mercury with a special microbalance. As it was not possible to condense the supposed helide at the temperature of liquid air, the yield was increased by the use of various synthesisers, of which the most efficacious was a form of Siemens ozone-generator containing platinised asbestos, the optimum gas pressure being 6 mm. Although the compound was rapidly resolved into its constituents by an intense beam of ultra-violet light, an expected absorption line was twice obtained, whilst further evidence confirming the synthesis was obtained from interferometer measurements.[25]

While the above work is obviously of a preliminary nature and should be received with caution, the formation of compounds corresponding with the hydrides appears possible on the assumption that the helium can exist in a hydrogen-like form, in which one electron is relatively far from the nucleus [26] and the scintillations observed in a zinc sulphide screen after helium had been passed over a radioactive deposit in a high-frequency discharge-tube may be attributed to this cause, and not to radium emanation or impurities in the gas. Further development of these new attacks on the "inert" gases will be awaited with interest.

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[23] W. H. Keesom and M. Wolfke, *Compt. rend.*, 1927, **185**, 1465; **A.**, 1928, 469; *idem*, *Proc. K. Akad. Wetensch. Amsterdam*, 1928, **31**, 90; **A.**, 696.

[24] L. I. Dana and H. K. Onnes, *ibid.*, 1926, **29**, 1060; **A.**, 1927, 101.

[25] J. J. Manley, *Phil. Mag.*, 1927, vii, **4**, 699; **A.**, 1928, 256.

[26] D. M. Morrison, *Proc. Camb. Phil. Soc.*, 1928, **24**, 268; **A.**, 684.

Group I.

Investigations of the action of hydrogen under pressure[27] have been extended to aqueous solutions of lead nitrate: reaction commences at 130—150°, and at 250° a series of basic salts are produced along with increasing proportions of lead oxide as the temperature is raised. The hydrolysis liberates nitric acid, but this does not accumulate in the solution since it is reduced by hydrogen: thus the previous addition of nitric acid merely delays the reactions but does not affect the ultimate products. Gold surfaces accelerate the reduction of nitric acid: hence in gold tubes at 250° and 80 atm. initial pressure, crystalline, blood-red lead oxide, *d* 8·59—8·79, is produced, whereas in quartz tubes under similar conditions the requisite temperature is 300° or more. At 260—270° in quartz tubes yellow lead oxide is formed in thin, crystalline leaflets, whilst at 300° and 200 atm. initial pressure colourless lead oxide results. The separation of metallic lead occurs at 250—275° and upwards, according to pressure. Water in the absence of hydrogen has no appreciable action on the precipitates.[28]

From a comparison of the densities of the hydrides of sodium, *d* 1·38, potassium, *d* 1·47, rubidium, *d* 2·60, and cæsium, *d* 3·42, with those of the respective metals, it appears that union with hydrogen causes a contraction of the metal lattice which increases with the atomic volume of the metal. This effect is even more pronounced in this case than with the hydrides of the alkaline-earth metals, but in both groups the molecular volumes approximate to those of the corresponding fluorides, and the lattices may be assumed to be of the rock-salt type.[29] The heats of formation of the hydrides of cerium, praseodymium, and lanthanum have been shown to differ very little from those of the alkaline-earth compounds, but whereas the latter substances are considerably denser than the corresponding metals, the reverse is true of the hydrides of the rare earths and titanium, zirconium, and vanadium, which show similarity in several ways and are by their semi-metallic nature at once sharply differentiated from the salt-like hydrides formed by elements of the first and second groups and from the metallic hydrides of the metals of Group VIII.[30]

Pure hydrogen peroxide has $d^{0°}$ 1·4649, whilst for solutions containing $A\%$ by weight $d = 0{\cdot}9486 + 0{\cdot}005163A$, provided A is 95 or more. The pure liquid shows a great tendency to supercool and for correct determination of the m. p. (– 0·89°) must be kept within 0·1° below that temperature and continuously stirred.[31]

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[27] *Ann. Reports*, 1926, **23**, 53; 1927, **24**, 42.

[28] V. Ipatiev and V. Ipatiev, jun., *Ber.*, 1928, **61**, [*B*], 624; **A.**, 603.

[29] M. Proskurnin and J. Kasarnovski, *Z. anorg. Chem.*, 1928, **170**, 301; **A.**, 697.

[30] A. Sieverts and A. Gotta, *Z. anorg. Chem.*, 1928, **172**, 1; **A.**, 712.

Anhydrous lithium sulphite has been isolated, the existence of the monohydrate confirmed, and derivatives with acetone, acetaldehyde, and benzaldehyde prepared; but all attempts to isolate the hydrogen sulphite have been unsuccessful.[32]

The chemiluminescent combination of sodium vapour with chlorine at pressures of about 10^{-3} mm. has been studied by allowing the vapour and the gas to stream into the opposite ends of a tube 100 cm. × 3 cm., whereupon reaction took place over 10—20 cm. of the tube length with the deposition of sodium chloride which was collected on a series of adjacent glass rings. At the pressures used, each molecular encounter resulted in reaction, so the reaction velocity could be calculated from the precipitate distribution. The corresponding light distribution along the reaction zone was determined photographically, and the efficiency calculated by comparing this distribution with the reaction-rate distribution. It is concluded that the reaction occurs in the gas phase, the primary reaction, $Na + Cl_2 \longrightarrow NaCl + Cl$, being non-luminescent; the emission arises from the secondary reaction, $Na_2 + Cl \longrightarrow NaCl + Na$, in which the NaCl molecule retains the reaction energy, and by collision transmits this energy to a free sodium atom. It is estimated that the second reaction proceeds 1000 times faster than the first.[33]

A most interesting piece of work [34] on the isotopes of potassium has been reported, affording evidence that, of the isotopes of potassium, K^{41} is mainly, if not wholly responsible for the radioactivity of the element. The matter is dealt with fully in the Report on Radioactivity,[35] but it may here be recorded that if this conclusion is correct the β-ray change of potassium will give rise to an isotope of calcium, Ca^{41}, which should be present in detectable amounts in potassium minerals.

Determinations of the vapour density of potassium at 950° by a special modification of the Victor Meyer method have shown that the ratio $[K_2]/[K]$ does not exceed 5×10^{-2}; hence it appears that the alkali metals probably contain only about 2% of diatomic molecules at their boiling points. Following a re-examination of the band spectra of these metals, absorption spectra of their mixed vapours were obtained, and as metals having a measurable proportion of polyatomic molecules show bands in their absorption spectra, the bands here found afford evidence that the alkali metals form a complete series of binary molecules with each other in the vapour state.[36]

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[31] A. C. Cuthbertson, G. L. Matheson, and O. Maas, *J. Amer. Chem. Soc.*, 1928, **50**, 1120; **A.**, 577.

[32] J. A. N. Friend and D. W. Pounder, *J.*, 1928, 2245; **A.**, 1103.

[33] H. Beutler and M. Pólányi, *Z. Physik*, 1928, **47**, 379; **A.**, 491.

[34] G. von Hevesy, *Nature*, 1927, **120**, 838; **A.**, 1928, 4; G. von Hevesy and M. Lögstrup, *Z. anorg. Chem.*, 1928, **171**, 1; **A.**, 684; M. Biltz and H. Zeigert, *Physikal. Z.*, 1928, **29**, 197; **A.**, 454.

[35] See p. 308.

In the presence of cupric oxide as catalyst mixed with potassium or sodium hydroxide, potassium nitrate may be reduced to nitrite by hydrogen at 440—480° or by carbon monoxide or water gas at 220—400°, the yields being 96, 65—70, and 70—75% respectively of the theoretical amount.[37]

If copper is heated with twice its weight of sulphuric acid at 130—170° the chief reaction is $6Cu + 6H_2SO_4 \longrightarrow 4CuSO_4 + Cu_2S + SO_2 + 6H_2O$,[38] whilst at 270° with excess of acid the reaction is $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$.[39]

A careful investigation has been made of the solubility of hydrogen in silver foil (0·40 and 0·12 mm. thick) between the temperatures 200° and 900° and at pressures from 5—80 cm. Below 400° the solubility is extremely small; the absorption Q increases rapidly with rising temperature, the values of log Q being practically a linear function of temperature, whilst at constant temperature the ratio $\sqrt{P}/Q$ is a constant. From Henry's law it follows that the dissolved gas must be dissociated into atoms, or else it must exist in the form of a dissolved hydride containing one atom of hydrogen to the molecule.[40]

Electrolysis of concentrated silver fluoride solutions with high current density yields at the cathode pure silver, whereas with low current density pure crystalline silver subfluoride, *d* 8·57, is obtained, which is decomposed by water into silver and silver fluoride but is unattacked by concentrated silver fluoride solutions. When heated, even in the complete absence of water, silver subfluoride decomposes to pure silver and fluorine and thus furnishes a method for the preparation of fluorine. The subfluoride crystals conduct electricity, and in contact with silver wire act as rectifiers.[41]

By electrolysis, using platinum electrodes in a divided cell with 8—10% solution of silver nitrate containing 40% of pyridine as anolyte and 10—15% sulphuric acid as catholyte,[42] an unstable, orange-red crystalline compound, $Ag(NO_3)_2,4C_5H_5N$, is produced in small yield, the silver being bivalent. It liberates iodine from potassium iodide and oxidises chromium and manganous salts to the chromic and permanganic condition.

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[36] J. M. Walter and S. Barratt, *Proc. Roy. Soc.*, 1928, [*A*], **119**, 257; **A.**, 812.

[37] J. Milbauer and V. Judenič, *Chem. Obzor.*, 1926, **1**, 16; *idem*, *Chem. Zentr.*, 1927, ii, 1338; **A.**, 1928, 252.

[38] J. G. F. Druce, *Chem. News*, 1928, **136**, 81; **A.**, 378.

[39] G. Fowles, *ibid.*, p. 257; **A.**, 602.

[40] E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc.*, 1928, [*A*], **117**, 662; **A.**, 229.

[41] A. Hettich, *Z. anorg. Chem.*, 1927, **167**, 67; **A.**, 1927, 1155.

[42] G. A. Barbieri, *Ber.*, 1927, **60**, [*B*], 2424; **A.**, 1928, 139.

A series of double thiosulphates of silver with the alkali metals and ammonium has been prepared by the gradual addition of aqueous silver nitrate to an ice-cold, well-agitated solution of the appropriate thiosulphate. The sparingly soluble compounds separate directly from the mixture, whilst the more freely soluble may be precipitated by the addition of alcohol.[43]

When a dilute solution of silver nitrate is treated with sodium carbonate and potassium persulphate at 70—80° silver peroxide is precipitated; in the presence of an iodate, almost homogeneous silver periodate, Ag_3IO_5, is nearly quantitatively precipitated in place of the oxide.[44]

Group II.

A new, simple, and direct method of purifying beryllium will be welcomed by those who have tried the older methods. The powdered oxide is placed between two perforated plates in a silica tube and heated in a current of carbonyl chloride at 450° for 1—2 hrs., whereby iron and aluminium are removed as volatile chlorides. Calcium chloride and any beryllium chloride may then be removed by washing with water, and the residue is pure beryllium oxide.[45] By dissolving beryllium in a liquid ammonia solution of potassium, a potassium ammonoberyllate [empirically $KBe(NH_2)_3$] is obtained as a colourless solid vigorously hydrolysed by water and resembling the corresponding aluminate rather than the magnesiate: a sodium salt may be similarly obtained. Beryllium cleansed with a liquid ammonia solution of ammonium chloride is insoluble in pure liquid ammonia but dissolves slowly when sulphur is present in solution, forming a yellow precipitate of ammoniated beryllium mono- or poly-sulphide.[46] Ammoniated beryllium halides, $BeCl_2,4NH_3$, $BeCl_2,2NH_3$, and $BeBr_2,4NH_3$, have been obtained by dissolving beryllium in liquid ammonia containing an excess of ammonium halide, whilst ammonobasic beryllium salts,

$$3Be(NH_2)_2,BeI_2,4NH_3,\ 3Be(NH_2)_2,BeBr_2,4NH_3,$$
$$3Be(NH_2)_2,BeBr_2,8NH_3,\text{ and }5Be(NH_2)_2,BeI_2,4NH_3,$$

have been prepared by the action of liquid ammonia solutions of normal beryllium halides on metallic beryllium.[47]

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[43] A. Rosenheim and G. Trewendt, *Ber.*, 1928, **61**, [*B*], 1731; **A.**, 1199.

[44] G. A. Barbieri, *Ber.*, 1927, **60**, [*B*], 2427; **A.**, 1928, 142.

[45] E. Chauvenet and E. Duchemin, *Compt. rend.*, 1927, **185**, 716; **A.**, 1927, 1155.

[46] F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1928, **50**, 652; **A.**, 493.

[47] *Idem, ibid.*, p. 657; **A.**, 493.

Calcium carbide reacts slowly at the ordinary temperature with bromine, about 80—90% of the carbon being converted into hexabromoethane after 3·5 months, but at higher temperatures free carbon only is formed. Chlorine at the ordinary temperature yields 3—5% of hexachloroethane, further attack probably being prevented by the layer of calcium chloride formed on the surface of the carbide. Very little reaction occurs with iodine at the ordinary temperature, but 35—37% of tetraiodoethylene, together with considerable amounts of free carbon, are obtained after heating at 100—160° in sealed tubes for some hours. A 20% yield of carbon disulphide and much carbon are obtained when calcium carbide and sulphur are heated at 270°, but only traces of the disulphide are formed at 500°. It is suggested that these reactions are preceded by adsorption and begin with the formation of calcium halide or sulphide and carbon; the carbon may then either polymerise or react further to form halogen compounds or carbon disulphide. The yields are determined by the ratio of the three reactions concerned, for if polymerised carbon accumulates, the carbide becomes coated with a layer of carbon and the first reaction is prevented.[48]

The reaction of calcium with nitrogen is autocatalytic and is most rapid with the finely divided metal such as results from the decomposition of calcium hexammine at low temperature and pressure. The speed of the reaction rises to a maximum at 450°, falls to zero at 600°, and increases again beyond the melting point of calcium. Except at low temperatures, in which case there is a deficit of 2—3%, the amount of nitrogen fixed corresponds with the formula Ca_3N_2, and the pressure of nitrogen evolved on reheating is highest if the original nitride is prepared at a low temperature, if reheating is rapid, and if the time between the two operations is short. The nitride may be black, bluish-black, reddish-brown, green, or yellow, according as it is prepared at 350°, 350—600°, 600—850°, 850—1100°, or above 1100°, respectively, and each type has a particular dissociation pressure, the dissociation of the yellow variety alone being reversible. The black nitride is pyrophoric. These phenomena may be explained by the assumption that the unstable combination CaN is formed at low temperatures and then decomposes irreversibly.[49]

The dissociation pressure of strontium carbonate lies on a curve similar to and between the curves for calcium and barium carbonates. Extrapolation gives 1258° as the temperature at which the dissociation pressure is one atmosphere. No evidence of the existence of a basic carbonate has been found.[50] Hydrogen chloride diminishes the solubility of radium chloride to a greater extent than that of barium chloride, whilst radium chloride does not influence appreciably the solubility of the barium salt. These facts underlie an industrial treatment of certain ores whereby the saturated solution of mixed chlorides is saturated with hydrogen chloride and the precipitate so obtained, containing all the barium and radium, is subjected to a fractional precipitation by the same means.[51]

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[48] E. Biesalski and H. van Eck, *Z. angew. Chem.*, 1928, **41**, 720; **A.**, 852.

[49] P. Dutoit and A. Schnorf, *Compt. rend.*, 1928, **187**, 300; **A.**, 1103.

[50] E. O. Jones and M. L. Becker, *J.*, 1927, **2669**; **A.**, 1928, **19**.

The existence of a transition point in zinc at 175° has now been confirmed by microscopical examination.[52]

The white additive compound, $3HgI_2,4NH_3$, produced by the action of excess of ammonia on $HgI_2,2NH_3$, dissolved in 10% ammonia at 21° deposits microscopic dark purple crystals of $Hg_9N_4I_6$ by the reaction $3(3HgI_2,4NH_3) + nNH_3 \longrightarrow Hg_9N_4I_6 + 12NH_4I + (n - 4)NH_3$.[53] Mercury reacts vigorously with ammonium persulphate in concentrated ammonia solution with the formation of mercuric tetramminopersulphate, $[Hg^{II}(NH_3)_4]S_2O_8$, which loses ammonia in air but can be recrystallised from concentrated ammonia solution.[54]

Group III.

Boric oxide, prepared by dehydrating boric acid below 800°, pouring into carbon tetrachloride at 0°, and powdering, is a rapid and efficient drying agent until it has absorbed 25% of its weight of water, corresponding to the formation of metaboric acid. If the dehydration temperature exceeds 800°, the product exhibits an induction period which is probably due to the formation of molecular complexes.[55]

The critical temperature of boron trichloride, previously undetermined, is given as $178{\cdot}8° \pm 0{\cdot}2°$.[56]

Work on boric acid and the alkali perborates previously reported[57] has been continued with special reference to the solid alkali perborates. By the addition of ethyl alcohol to a solution of lithium monoborate and hydrogen peroxide, lithium perborate, $LiBO_3,2H_2O$ or $LiBO_2,H_2O_2,H_2O$, was precipitated, from which, by recrystallisation from water or by careful dehydration, the lower hydrate, $LiBO_3,H_2O$ or $LiBO_2,H_2O_2$, was obtained. Further dehydration by heating at

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[51] A. G. Eliseev, *Ann. Inst. Anal. Physico-Chim. Leningrad*, 1926, **3**, 443; **A.**, 1928, 31.

[52] G. I. Petrenko, *Z. anorg. Chem.*, 1927, **167**, 411; **A.**, 1928, 10.

[53] M. François, *Compt. rend.*, 1928, **186**, 1205; **A.**, 603.

[54] F. Fichter and S. Stern, *Helv. Chim. Acta*, 1928, **11**, 754; **A.**, 971.

[55] J. H. Walton and C. K. Rosenbaum, *J. Amer. Chem. Soc.*, 1928, **50**, 1648; **A.**, 852.

[56] T. W. Parker and P. L. Robinson, *J.*, 1927, 2977; **A.**, 1928, 114.

[57] *Ann. Reports*, 1927, **24**, 48.

100° in a vacuum causes the substance to lose active oxygen, and simultaneously to acquire the property of reacting with water with the liberation of oxygen, possibly owing to the formation of $(LiBO_2)_2,O_2$, and ultimately the monoborate remains. The complete change in crystal structure attending the formation of the monoborate suggests that the original compound cannot be regarded merely as monoborate with hydrogen peroxide of crystallisation. Ammonium and potassium perborates apparently exist only as hemihydrates, $KBO_3,0{\cdot}5H_2O$, and attempts to remove this water by heating lead to their decomposition, as with the lithium salt. It is inferred that the only true alkali perborate is the anhydrous sodium salt containing a boron atom with the co-ordination number 3; the other alkali perborates are regarded as salts of dibasic acids containing two boron atoms with the co-ordination number 4, the lithium and hydrated sodium salts having the formula $M_2(B_2O_6,2H_2O)$ and the potassium and ammonium salts $M_2(B_2O_6,H_2O)$.[58]

Silver ultramarine, $Ag_6Al_6Si_6O_{30}S_3$, is obtained by heating silver nitrate in a sealed tube at 120—130° with ultramarine. From this product a series of alkali, alkaline-earth, and even alkyl (*n*-butyl) ultramarines has been prepared by heating it with solutions of the appropriate chlorides or, preferably, iodides.[59]

A description has been given of the preparation of the indium oxides: In_2O_3 by igniting the hydroxide to constant weight, In_2O by the action of a reducing gas at 500° on In_2O_3 followed by sublimation in a high vacuum at 650—750°, and InO as a residue from the last operation.[60] The properties of these oxides are recorded, and also the preparation and properties of the corresponding sulphides.

The problem of the molecular structure of thallium tri-iodide has been investigated by examining (*a*) its reactions in methyl alcohol or acetonitrile, in which it exhibits the general reactions of a thallic salt, and (*b*) the absorption spectra of the tri-iodide and several additive compounds, which all show two bands separated by 1400 Å.U., whereas substances containing the tri-iodide ion give two bands separated by 650—720 Å.U. It is inferred that in thallium tri-iodide the iodine atoms are not present as a tri-iodide ion, but are joined, at least in part, by covalent linkages directly to the metal.[61]

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[58] H. Menzel (with J. Meckwitz and W. Kretzschmar), *Z. anorg. Chem.*, 1927, **167**, 193; **A.**, 1928, 32.

[59] F. M. Jaeger and F. A. van Melle, *Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30**, 885; **A.**, 1928, 463.

[60] A. Thiel and H. Luckmann, *Z. anorg. Chem.*, 1928, **172**, 353; **A.**, 852.

[61] A. J. Berry and T. M. Lowry [with (Mrs.) R. R. Goldstein and F. L. Gilbert], *J.*, 1928, 1748; **A.**, 1071.

The Rare Earths.

From a consideration of solubility data and of the magnetic ionic moments as a function of the number of electrons in the tervalent ion, the rare-earth metals are inserted in the periodic table as follows :

Series.	Group II.		Group III.		Group IV.		Group V.
	A.	B.	A.	B.	A.	B.	A.
7		Cd		In		Sn	
8	Ba		**La**		**Ce, Pr, Nd, Il**		
9				**Sa, Eu, Gd**		**Tb**	
10			**Dy, Ho, Er,** **Tu, Yb, Lu**		Hf		Ta
11		Hg		Tl		Pb	

It is claimed that this scheme places the whole of the elements of the rare-earth group into Mendeléev's periodic system without destroying its symmetry or impairing its utility in the slightest, and that whilst rigorous testing is difficult because of the lack of many essential data, a broad line taken through those available confirms, in general, the proposed arrangement. It will be remarked that the new arrangement does not change the position of the rare earths in the table as usually accepted but simply gives a more detailed statement of their distribution in that position.[62]

An attempt has been made to determine the analogies which exist between the compounds of scandium and those of other tervalent elements, the iron and the rare-earth groups. In the solubility of its salts it resembles the elements of the rare earths, but it also exhibits many close analogies with the iron group; thus the acetylacetonates are isomorphous with those of iron, and the double alkali sulphates with those of aluminium, whilst it forms a series of double alkali sulphates corresponding with the anhydrous alums, which are quite unknown in the rare-earth series; its basic nitrates closely resemble those of chromium. Spectroscopic evidence using the acetylacetonates confirms its relationship with the aluminium family. No such intimate relationship is found, however, between the simple salts of scandium and those of either the rare-earth or the iron group of elements, scandium occupying a transitional position between the two groups. A study of numerous new salts of gadolinium and europium, similarly directed, shows that these elements resemble both the cerium and yttrium groups of the rare-earth elements and form a transition between the two groups.[63]

The use of perchloric acid, in preference to nitric acid, in the separation of various members of the rare-earth group has been advocated, and a number of perchlorates and hexa-antipyrineperchlorates have been prepared and described.[64]

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[62] J. F. Spencer, *J. Amer. Chem. Soc.*, 1928, **50**, 264; **A.**, 461.

[63] P. B. Sarkar, *Ann. Chim.*, 1927, [x], **8**, 207; **A.**, 1928, 32.

The anhydrous chlorides of lanthanum, cerous cerium, praseodymium, neodymium, samarium, dysprosium, yttrium, holmium, and thulium have been prepared by dehydrating the hexahydrates at 100—200° in a stream of hydrogen chloride under reduced pressure. Melting points, densities, and p_H values in solution have been recorded,[65] the last confirming (except in the case of dysprosium, which appears more basic) the order of basicity given by Hopkins.

Neodymium selenate and its penta- and octa-hydrates have been prepared, and evidence of the existence of a dodecahydrate has been obtained.[66]

Work on the displacement of spectra occurring during compound formation has been continued.[67] It is based on the hypothesis that the electrostatic attraction of the kation for electrons of the remaining sheaths becomes more pronounced when the anion involves the valency electrons of the kation with greater intensity and consequently draws these sheaths towards the nucleus : hence contraction occurs, the paths of the vibrating electrons becoming shorter, light of a shorter wave-length is emitted, and a displacement of the spectrum towards the ultra-violet takes place. This displacement is very marked in the series anhydrous iodide, bromide, chloride, and fluoride of praseodymium. Since the anhydrous compounds can unite with water, ammonia, etc., by means of residual affinities, the atom does not exert its full chemical affinity in them. This is, however, fully displayed in solution, when the atom is freed from the circle of restricting atoms, and the contraction thereby caused explains the observed displacement of the spectrum towards the violet. Another aspect of the matter is that the lessened importance of the anion, by reason of electrolytic dissociation, accounts for the disappearance of the difference in position of the lines observed in the solid salts.[68] This interesting inquiry has been further extended to praseodymium salts of oxygenated acids, the observations on which tend to support the foregoing hypothesis.[69]

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[64] E. Wilke-Dörfurt and O. Schliephake, *Z. anorg. Chem.*, 1928, **170**, 129; **A.**, 494.

[65] J. H. Kleinheksel and H. C. Kremers, *J. Amer. Chem. Soc.*, 1928, **50**, 959; **A.**, 603.

[66] J. A. N. Friend and A. A. Round, *J.*, 1928, 1820; **A.**, 972.

[67] F. Ephraim and R. Bloch, *Ber.*, 1926, **59**, [*B*], 2692; **A.**, 1927, 121.

[68] *Idem, ibid.*, 1928, **61**, [*B*], 65; **A.**, 217.

[69] *Idem, idid.*, p. 72; **A.**, 217.

Group IV.

Graphitic acid, prepared from Ceylon graphite, is crystalline and has a well-defined *X*-ray spectrum somewhat similar to that of graphite. When heated cautiously to about 200° it decomposes explosively, yielding incipiently crystalline, voluminous " carbon I," which differs from graphite in the closer proximity of the interference lines (002) and (111). Decomposition at 200° under pressure gives the more distinctly crystalline " carbon II " having a spectrum closely approximating to that of lustre carbon prepared at 900°, except that again the same interference lines are closer, whilst decomposition under sulphuric acid at 150° produces the more highly crystalline " carbon III," in which the arrangement is similar to that in retort graphite. These products from graphitic acid differ from lustre carbon and retort graphite in the remarkable sharpness of their interferences.[70]

By shaking carbon disulphide with 0·8% sodium amalgam, extracting the product with 90% alcohol, and treating the extract with methyl sulphate, it has been possible to obtain : methyl tetrathio-oxalate, $(CS{\cdot}SMe)_2$, m. p. 100·9°, b. p. 210°/0·1 mm. (decomp.), $d_4^{20°}$ 1·619, hydrolysed to oxalic acid; methyl methylxanthate, $C_3H_6OS_2$, b. p. 168°/765 mm., converted by alcoholic ammonia into ammonium thiocyanate; methyl trithiocarbonate, b. p. 224°/760; an isomeric methyl tetrathio-oxalate, m. p. 71·6°, $d_4^{20°}$ 1·658, apparently stereoisomeric with that described above; tetramethylthiolethylene, $(SMe)_2C{:}C(SMe)_2$, m. p. 61·5°, $d_4^{18°}$ 1·397, which gives a corresponding bromo-derivative, $C_6H_{12}Br_4S_4$. The production of methyl methylxanthate is due to a subsidiary reaction, since the compound is not produced when the crude product of the reaction is treated directly with methyl sulphate. Carbon disulphide appears to be able to combine additively with sodium, giving $\cdot CS{\cdot}SNa$ and $:C(SNa)_2$, but the mechanism is not yet explained. A solution of sodium in liquid ammonia reacts vigorously with carbon disulphide, producing a brown mass which, with methyl sulphate, yields methyl tetrathio-oxalate, methyl trithiocarbonate, tetramethylthiolethylene, and methyl sulphide.[71]

Solid azido-carbon disulphide reacts explosively with chlorine and bromine, although not with iodine. By carrying out the former reactions in cooled, non-aqueous solutions, the monohalogenoazidodithiocarbonates, $XS{\cdot}CS{\cdot}N_3$, are probably produced, whilst by the action of bromine in ethereal solution on silver azidodithiocarbonate the tribromo-derivative results, $Br_3S{\cdot}CS{\cdot}N_3$. On hydrolysis with potassium hydroxide, the monobromo-compound gives potassium azidothiocarbonate, $KS{\cdot}CS{\cdot}N_3$, and this salt in concentrated aqueous solution gives immediately with iodine a heavy black oil.[72]

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[70] U. Hofmann, *Ber.*, 1928, **61**, [*B*], 435; **A.**, 379.

[71] B. Fetkenheuer (with H. Fetkenheuer and H. Lecus), *Ber.*, 1927, **60**, [*B*], 2528; **A.**, 1928, 141.

The thermal equilibrium of carbonyl bromide even at the ordinary temperature lies well in favour of the components and is attained very slowly from carbon monoxide and bromine, but the compound may readily be prepared by heating a mixture of carbon tetrabromide and concentrated sulphuric acid (*d* 1·83) at 150—170°, and purifying the distillate by two distillations following treatments with mercury and powdered antimony, respectively. The colourless liquid, d^{15° 2·52, is stable up to about 150°, is less readily hydrolysed by water than the corresponding chloride, and has a similar physiological action.[73]

A number of water-soluble salts are insoluble in acetic acid, and in this solvent, as double decomposition occurs as readily as in water, certain sulphates which normally form hydrates can be precipitated in the anhydrous condition. Certain metal acetates behave in acetic acid as do the corresponding bases in water; thus zinc acetate is insoluble but dissolves readily when sodium acetate is added.[74]

The statement that ultra-violet absorption spectra indicate the formation of considerable quantities of gaseous silicon monoxide during the reduction of the dioxide by carbon at 1500° is of interest as being, apparently, the first evidence for the existence of a lower oxide.[75]

Melts of the composition $Na_4S_3O_8$ (orthotrisilicate) and $Na_2Si_2O_7$ (metatrisilicate) give on crystallisation $Na_2SiO_3 + Na_2Si_2O_5$ and $Na_2Si_2O_5 + SiO_2$, respectively; the dehydration of silica gel by acetone indicates the presence only of $H_2Si_2O_5$; and the precipitation of sodium metasilicate, disilicate, or hydrogen silicate with barium chloride gives a mixture of barium metasilicate and disilicate except in the presence of large excess of sodium hydroxide, in which case the former only is produced. From these facts it is inferred that SiO_3'' and Si_2O_5'' are the only anions present in solutions of alkali silicates, and that the equilibrium is usually largely in favour of the disilicate ion.[76] A similar inference is drawn from the exhaustive extraction of water from preparations of hydrated silica with liquid ammonia in a special extraction apparatus. For metasilicic acid, the product has the composition $6SiO_2,2H_2O,4NH_3$ at $-78{\cdot}5°$, but with rise of temperature it loses ammonia in stages of one molecule, yielding finally $6SiO_2,2H_2O,NH_3$, stable at the ordinary temperature. These results support the view that the minimum molecular formula for the acid is $6SiO_2,6H_2O$. Partly dehydrated metasilicic acid preparations give the same compounds, whilst disilicic acid yields the product $2SiO_2,H_2O,NH_3$, which, since it loses ammonia in a continuous and not a step-wise manner when examined in the tensimeter, gives no evidence that the acid is more complex than $2SiO_2,H_2O$. Similar experiments with preparations having the composition of "granitic" (orthotrisilicic) and metatrisilicic acids (respectively, $3SiO_2,2H_2O$ and $3SiO_2,H_2O$) indicate that these are not definite compounds, and *X*-ray examination supports this view.[77]

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[72] W. H. Gardner and A. W. Browne, *J. Amer. Chem. Soc.*, 1927, **49**, 2759; **A.**, 1928, 34.

[73] S. Lenher and H. J. Schumacher, *Z. physikal. Chem.*, 1928, **135**, 85; **A.**, 847; H. J. Schumacher and S. Lenher, *Ber.*, 1928, **61**, [*B*], 1671; **A.**, 1200.

[74] A. W. Davidson, *J. Amer. Chem. Soc.*, 1928, **50**, 1890; **A.**, 947.

[75] K. F. Bonhoeffer, *Z. physikal. Chem.*, 1928, **131**, 363; **A.**, 379.

[76] R. Schwarz and H. Richter, *Ber.*, 1927, **60**, [*B*], 2263; **A.**, 1928, 33.

Well-defined substitution products, monoacetatomonoiodosiloxen, $Si_6O_3H_4I(OAc)$, and diacetatodibromosiloxen, $Si_6O_3H_2Br_2(OAc)_2$, have been prepared by adding to siloxen successive small amounts of a solution of the halogen in acetic anhydride, and removing the liquid phase from the solids in the reacting system before each new addition of halogen; otherwise, with bromine, only $Si_6O_3H_3Br_2(OAc)$ is formed. Brominating in carbon disulphide and removing the hydrogen bromide yields successively tetrabromosiloxen, $Si_6O_3H_2Br_4$, and hexabromosiloxen, $Si_6O_3Br_6$. These compounds are all yellowish solids of unknown constitution.[78] By their regulated hydrolysis with 80% alcohol, or by the action of sulphur dioxide dissolved in acetone, the following hydroxysiloxens are obtained: Mono- [$Si_6O_3H_5{\cdot}OH$, yellow], di- [$Si_6O_3H_4(OH)_2$, brownish-red], tri- [$Si_6O_3H_3(OH)_3$, red], tetra- [$Si_6O_3H_2(OH)_4$, brownish-violet], and hexa- [$Si_6O_3(OH)_6$, black]. Hexahydroxysiloxen is extremely explosive in air, this tendency increasing in these compounds with increasing number of SiOH groups and Si–Si linkings.[79]

Germanium tetrafluoride is best obtained by the thermal decomposition of pure barium fluogermanate, prepared by dissolving germanium oxide in 48% hydrofluoric acid solution and adding a saturated solution of the theoretical quantity of barium chloride; the granular precipitate, after drying at 120°, rapidly evolves gas when heated at 700°. The product, purified by fractional distillation at $-104°$, is a colourless, fuming gas, condensable at the temperature of liquid air to a mass of white crystals which sublime when the temperature is allowed to rise. Liquid germanium tetrafluoride exists at −15° under its own vapour pressure of 3032 mm. When passed into water, the gas yields at first a clear acid solution (from which potassium hydroxide precipitates potassium fluogermanate) and later a gelatinous precipitate of hydrated germanium dioxide separates. Glass in presence of moisture is rapidly etched by the gas, but quartz is not attacked below 700°, nor is there any evidence of dissociation at 1000°.[80]

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[77] W. Biltz, *Z. Elektrochem.*, 1927, **33**, 491; **A.**, 379; W. Biltz and E. Rahlfs, *Z. anorg. Chem.*, 1928, **172**, 273; **A.**, 854.

[78] H. Kautsky and A. Hirsch, *ibid.*, **170**, 1; **A.**, 495.

[79] H. Kautsky and H. Thiele, *ibid.*, **173**, 115; **A.**, 854.

Attempts to prepare germanium dichloride by reduction of the tetrachloride and other methods have failed, but reduction of a mixture of germanobromoform and germanium tetrabromide by zinc gives the dibromide as a colourless crystalline solid, which decomposes ($2GeBr_2 = Ge + GeBr_4$) when heated, is insoluble in hydrocarbons, is soluble in alcohol and acetone, and is hydrolysed by water to yellow, hydrated germanous hydroxide. It absorbs bromine to form the tetrabromide, and with hydrogen bromide yields germanobromoform (m. p. −24° approx.). The di-iodide, obtained by the action of concentrated hydriodic acid on an excess of a mixture of hydrated mono- and di-oxides of germanium below 40°, is a yellow solid crystallographically similar to lead iodide; its solutions possess reducing properties; and on heating in a vacuum it yields germanium and the tetraiodide.[81]

The optimum temperature for the reduction of germanium disulphide to the monosulphide in a current of hydrogen is about 480°. The very hard, black crystals of the monosulphide are practically insoluble in mineral acids, but are dissolved by fused potassium hydroxide or by prolonged digestion with aqueous potassium hydroxide.[82] Reduction of germanic salts with zinc and 25% sulphuric acid produces brown germanous oxide, which is stable when dry and almost insoluble in hydrochloric acid. When, however, reduction is effected with hypophosphorous and hydrochloric acids at 100° for 2 hours, followed by neutralisation in the cold with ammonia an orange-yellow hydroxide is obtained, which is soluble in alkalis and hydrochloric acid. The hydrochloric acid solution yields the chloride ($GeCl_2$), which is hydrolysed by water to a white oxychloride, is a strong reducing agent, and gives with hydrogen sulphide the orange-red sulphide GeS.[83]

The densities of ordinary lead chloride and uranium lead chloride (Pb = 206·05) are $d_{4^\circ}^{18^\circ} = 5{\cdot}909 \pm 0{\cdot}001$ and $5{\cdot}884 \pm 0{\cdot}001$, respectively, whence the identical molecular volumes, 47·07 c.c., are calculated. The densities of the saturated aqueous solutions differ, but the molecular volumes of the salts in these solutions are again identical. Different increases in the refractive index of water are caused by the addition of equal weights of the two salts, but the molecular refractivities of the dissolved salts are identical. The equivalent conductivities of the almost saturated solutions are practically equal and the heats of precipitation of the chromates are identical.[84]

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[80] L. M. Dennis and A. W. Laubengayer, *Z. physikal. Chem.*, 1927, **130**, 520; **A.**, 1928, 33.

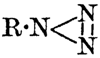
[81] F. M. Brewer and L. M. Dennis, *J. Physical Chem.*, 1927, **31**, 1526; **A.**, 1927, 1156.

[82] L. M. Dennis and S. M. Joseph, *ibid.*, p. 1716; **A.**, 1928, 33.

[83] J. Bardet and A. Tchakirian, *Compt. rend.*, 1928, **186**, 637; **A.**, 380.

Group V.

Nitrogen trifluoride has been obtained by electrolysing fused anhydrous ammonium hydrogen fluoride. It is a colourless gas at the ordinary temperature, and, according to analysis and density measurements, has the formula NF_3. It is condensed by liquid air to a colourless mobile liquid which boils under atmospheric pressure at −119° and freezes below −210°. Vapour-pressure measurements have been made between −125° and −194°, and the molecular heat of vaporisation is calculated to be 2400 g.-cal. Nitrogen trifluoride is insoluble in water and unattacked by water or hydrogen, but when sparks are passed through a mixture of the gas with water vapour, hydrogen fluoride and oxides of nitrogen are formed. With hydrogen under the same conditions the reaction is very violent, nitrogen and hydrogen fluoride being obtained. The gas is remarkably stable; it does not react with mercury, manganese dioxide, potassium hydroxide solution, or glass at the ordinary temperature.[85]

Determinations of the parachor of a number of derivatives of azoimide agree excellently with the calculated values for the cyclic form  $R\cdot N<\begin{matrix}N\\ \| \\ N\end{matrix}$ (if it be assumed that the double linking between nitrogen atoms has the same value as C:C and the triple linking the same effect as the acetylenic or C:N), and it appears that Thiele's formula, R·N:N:N, is probably untenable.[86]

Hydrazine is formed in appreciable quantities when pure aqueous ammonia is passed through a strongly cooled high-tension arc and then cooled at once with liquid air. It is suggested that the mechanism of this synthesis is the union of NH_3 and $-NH$, rather than the union of two NH_2 groups, because the probability of the latter collision is very small when ammonia is present in great excess.[87] Hydrazine hydrate and dilute selenic acid yield colourless hydrazine hydrogen selenate; the salt is stable in boiling water, but when dry it explodes with unusual readiness by heat, shock, or contact with hydrochloric acid vapour. A large number of crystalline compounds of hydrazine with metallic sulphites and nitrites have been prepared by the action of hydrazine hydrate on solutions of the metallic bisulphites [88] or on solutions of the acetates in presence of excess of sodium nitrite.

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[84] W. A. Roth and O. Schwartz, *Ber.*, 1928, **61**, [*B*], 1539; **A.**, 942.

[85] O. Ruff, J. Fischer, and F. Luft, *Z. anorg. Chem.*, 1928, **172**, 417; **A.**, 854.

[86] H. Lindemann and H. Thiele, *Ber.*, 1928, **61**, [*B*], 1529; **A.**, 937.

[87] G. Bredig and A. Koenig, *Naturwiss.*, 1928, **16**, 493; **A.**, 854.

The reaction of nitrogen peroxide with certain anilides indicates the constitution $O{:}N{\cdot}O{\cdot}NO_2$, whilst other reactions are consistent with the simple formula $O_2N{\cdot}NO_2$: it is therefore suggested that the liquid exists in these two tautomeric forms.[89]

The reducing action of magnesium amalgam on metallic nitrates and nitrites affords a convenient method for the preparation of hyponitrites. In general, magnesium amalgam is added slowly to a concentrated solution of the salt at 5° or below, the magnesium hydroxide being removed after a short time, and the reduction similarly repeated until the solution is free from nitrate and nitrite : it is then concentrated in a vacuum over sulphuric acid. A number of hyponitrites not hitherto described have thus been made, including the explosive oxyhyponitrite, $Cd(OH)NO$, whilst a 60% yield of hydroxylamine sulphate of 97·8% purity has been obtained by the reduction of nitric acid in the presence of sulphuric acid.[90]

Sodium hydronitrite, Na_2NO_2, having an intense yellow colour, has been prepared by the interaction of solutions of sodium nitrite and sodium in liquid ammonia,[91] and can be obtained also by substituting lithium or potassium for sodium in this reaction or by cathodic reduction of sodium nitrite in liquid ammonia in a divided cell. The alkali hydronitrites are stable when gently heated in a vacuum or in nitrogen, but at 100—130° decompose violently. Of particular interest is the fact that under certain conditions direct addition of oxygen to a hydronitrite may occur with formation of an unstable, brown peroxide (?) $(Na_2NO_2)_2{:}O_2$, which is decomposed by water into oxygen, sodium nitrite and hydroxide, and hydrogen peroxide. Similarly, an atom of iodine is taken up from an ethereal solution, giving a black additive product which rapidly decomposes into sodium nitrite and iodine. It appears probable that addition of sodium to sodium nitrite occurs at the oxygen rather than the nitrogen atom, and that the hydronitrites $-N(ONa)_2$ are thus analogous to Schlenk's metallic ketyls.

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[88] J. Meyer and W. Aulich, *Ber.*, 1928, **61**, [*B*], 1839; **A.**, 1200; P. Rây and B. K. Goswami, *Z. anorg. Chem.*, 1928, **168**, 329; **A.**, 258.

[89] M. Battegay and W. Kern, *Bull. Soc. chim.*, 1927, [iv], **41**, 1336; **A.**, 1928, 34.

[90] P. Neogi and B. L. Nandi, *J.*, 1928, 1449; **A.**, 855.

[91] E. Zintl and O. Kohn, *Ber.*, 1928, **61**, [*B*], 189; **A.**, 258.

Allotropic modifications of phosphorus obtained under high temperatures and pressures in nitrogen in contact with metallic powders have been described as consisting of purple (1·90, 4·4 mm., 200°), ruby (2·11, 1·4 mm., 346°), and black (2·7, $<$0·5 mm., 490°) forms, the figures in parentheses being the corresponding density, vapour pressure at 21°, and inflammation point, respectively. These and white phosphorus form a continuous series of solid solutions, red phosphorus being a mixture of ruby and purple phosphorus, and violet a mixture of the ruby and black varieties. Black and purple phosphorus form a eutectic.[92]

Hexafluorophosphoric acid, HPF_6, is formed by the hydrolysis of difluorophosphoric acid, HPO_2F_2, which is produced when phosphoric oxide is dissolved in 40% hydrofluoric acid. Solutions of the potassium salt give no precipitate with salts of the alkaline-earth or heavy metals. The PF'_6 ions are very stable towards boiling water and alkali hydroxide but are slowly decomposed by concentrated acids. Nitrosyl fluoride and phosphorus pentafluoride appear to yield the crystalline compound NOF_6.[93]

It has been shown that phosphorus trioxide, prepared by the method of Thorpe and Tutton, contains 1·5—2% of phosphorus, which may be eliminated by fractional crystallisation from carbon disulphide, exposure to light, and distillation. The pure oxide melts at 23·8°, is unaffected by sunlight, and does not glow or oxidise in moist or dry oxygen at the ordinary temperature.[94]

A series of sodium thiophosphates has been prepared by the action of sodium sulphide or hydrosulphide on phosphorus pentasulphide,[95] and improvements have been described in methods for the electrolytic preparation of perphosphates, resulting in the production of $Rb_4P_2O_8$, $Ag_4P_2O_8$(?), $Ba_2P_2O_8,4H_2O$, $Zn_2P_2O_8,4H_2O$, and $Pb_2P_2O_8$.[96]

Attempts have been made to increase the quantity of protoactinium (element 91) available and about 2 mg. of the oxide, apparently fairly pure, have been extracted from Joachimsthal pitchblende residues.[97] It is pointed out that such material would form a valuable source of actinium, besides affording means of studying the special chemical properties of elements of atomic number 91 in relation to those of the lower members of the same group, niobium and tantalum, and of the neighbouring elements uranium and thorium. Protoactinium is also interesting because elements of odd atomic number, especially in the last horizontal series of the periodic table, are comparatively rare.[98]

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[92] V. J. Nikolajev, *Compt. rend.*, 1928, **186**, 1621; **A.**, 827; V. Ipatiev and V. J. Nikolajev, *Ber.*, 1928, **61**, [*B*], 630; **A.**, 604.

[93] W. Lange, *ibid.*, p. 799; **A.**, 604.

[94] (Miss) C. C. Miller, *J.*, 1928, 1847; **A.**, 972.

[95] H. E. Wallsom, *Chem. News*, 1928, **136**, 113; **A.**, 380.

[96] F. Fichter and E. Gutzwiller, *Helv. Chim. Acta*, 1928, **11**, 323; **A.**, 489.

[97] A. von Grosse, *Ber.*, 1928, **61**, [*B*], 233; **A.**, 259.

Group VI.

The fact that the viscosity of sulphur is usually dependent on its previous thermal treatment is probably due to traces of sulphuric acid, hydrogen sulphide, or sulphur dioxide, which retard the attainment of inner equilibrium between the S_{μ} and S_{λ} varieties, for pure gas-free material, prepared by distillation in a stream of carbon dioxide, followed by distillation in a high vacuum, shows no such irregularity. From sulphur so purified, crystals of S_{III} (mother-of-pearl sulphur) separate readily, but rhombic sulphur could not be obtained. The natural f. p. was found to be 103·8—103·9° and the ideal m. p. about 107°, whilst the liquid could be supercooled to 80°, viscosity measurements being made at that temperature.[99]

The chlorides of zinc, aluminium, ferric iron, and bivalent mercury dissolve in liquid hydrogen sulphide, and the last-named is thiohydrolysed, depositing black mercuric sulphide which later turns red. A similar action occurs with cuprous and silver chlorides. Boron trichloride yields white crystals of $BCl_3,12H_2S$, carbon and silicon tetrachlorides are miscible without immediate reaction, and phosphorus, antimony, and bismuth trichlorides give rise to the following thio-salts: $PSCl_3$, $SbSCl_3$, and $BiSCl,BiCl_3$.[1] From the conductivity of solutions in hydrogen sulphide, particularly of iodine, it is concluded that the solvent is an ionising medium.[2]

Hydrogen pentasulphide has been prepared from pure ammonium pentasulphide by treatment with anhydrous formic acid: it is a thin, clear yellow oil, $d^{16°}$ 1·67, which on cooling becomes suddenly viscous at −25° and a glassy solid at −50°. It has also been shown that ammonium pentasulphide on distillation in a Faraday tube yields ammonium monosulphide, not the disulphide as was previously supposed, and evidence has been obtained that the alleged ammonium heptasulphide is a solid solution of sulphur in the pentasulphide. Thus there appears to be but one polysulphide of ammonium, the pentasulphide. By sublimation from a suspension of the pentasulphide in carbon disulphide, pure orange-yellow ammonium thiocarbonate is obtained,[3] from which it is possible to isolate trithiocarbonic acid, f. p. $-30{\cdot}5°$, $d_{4°}^{17°}$ 1·47, $\gamma^{12{\cdot}5°}$ 48·3 dynes/cm.

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[98] O. Hahn, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1927, 275; **A.**, 1928, 343.

[99] C. C. Farr and D. B. Macleod, *Proc. Roy. Soc.*, 1928, [*A*], **118**, 534; **A.**, 578.

[1] A. W. Ralston and J. A. Wilkinson, *J. Amer. Chem. Soc.*, 1928, **50**, 258; **A.**, 381.

[2] H. R. Chipman and D. McIntosh, *Proc. Nova Scotian Inst. Sci.*, 1927, **16**, 189; **A.**, 1928, 845.

Potassium hexathionate has been prepared by the addition of a solution of potassium nitrite (1 mol.) and potassium thiosulphate (3 mols.) to well-cooled hydrochloric acid. The mixture is vigorously shaken until the colour passes through brown and green to yellow, after which nitrous fumes are removed by a current of air. After the separation of precipitated potassium chloride the filtrate is concentrated under diminished pressure, and potassium hexathionate, mixed with chloride, separates. The hexathionate is stable when dry, but readily decomposes in aqueous solution; acids stabilise these solutions, and when much acid is present the hexathionate may be crystallised or salted out.[4]

Selenium tetrafluoride has been made by the action of selenium tetrachloride on silver fluoride.[5] The compound has *d* 2·77, b. p. 93°, and m. p. $-13{\cdot}2°$, and is thus distinct from the oxyfluoride, prepared [6] by using selenium oxychloride in a similar reaction at 140°, which has *d* 2·67, b. p. 121—129°, m. p. 4·6°. Both liquids attack silica and silicious materials with the formation of silicon tetrafluoride together with selenium or selenium dioxide or both.

An extended investigation has been made of the double salts of selenic acid, for details of which the original paper should be consulted.[7]

An acid molybdate solution reduced with zinc when saturated with hydrogen selenide deposits molybdenum pentaselenide, Mo_2Se_5; and the diselenide, $MoSe_2$, and sesquiselenide, Mo_2Se_3, have been prepared by dry methods. A solution of potassium molybdate in concentrated potassium hydroxide, when saturated with hydrogen selenide, deposits red needles of potassium selenomolybdate, K_2MoSe_4. The sodium salt cannot be similarly prepared, but glistening, blue crystals of $(NH_4)_2MoSe_4$ are obtained in this way from molybdic acid in concentrated ammonia.[8] Similar treatment of cold, concentrated ammonium tungstate solution with hydrogen selenide yields green orthorhombic crystals of ammonium selenotungstate, $(NH_4)_2WSe_4$, whilst incomplete saturation yields red, triclinic crystals of the diselenotungstate, $(NH_4)_2WSe_2O_2$.[9]

It is recorded that tellurium can be deposited in smooth, thick layers with theoretical current efficiency from a bath containing 300 g. of tellurium dioxide (49·6% TeO_2, 46·1% Na_2TeO_3), 500 g. of 48% hydrofluoric acid, and 200 g. of sulphuric acid per litre, 1·6 amp./dm.[2] being used at a lead cathode. With tellurium anodes this bath can be used for refining tellurium, all selenium remaining in the anode slimes.[10]

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[5] E. B. R. Prideaux and C. B. Cox, *J.*, 1928, 1603; **A.**, 855.

[6] *Idem, ibid.*, p. 738; **A.**, 495.

[7] J. Meyer and W. Aulich, *Z. anorg. Chem.*, 1928, **172**, 321; **A.**, 856.

[8] E. Wendehorst, *ibid.*, **173**, 268; **A.**, 973.

[9] V. Lenher and A. G. Fruehan, *J. Amer. Chem. Soc.*, 1927, **49**, 3076; **A.**, 1928, 142.

A heliotrope double chloride, $CrCl_3,HCl,xH_2O$ (where x is approximately 6), is precipitated by passing hydrogen chloride through a concentrated solution of green chromic chloride. The substance is insoluble in alcohol or ether, but in water gives a pink solution which immediately turns green.[11]

By the action of pure carbon monoxide for 6 hours at 0° on pure tungsten hexachloride in the presence of magnesium phenyl bromide, ether, and benzene, colourless laminated crystals of tungsten carbonyl, $W(CO)_6$, were obtained which sublimed at 50°, and were decomposed at 100° or by fuming nitric acid, but not by water or ordinary acids.[12]

Group VII.

Magnesium perchlorate is applied as a convenient drying agent by soaking pumice granules in a 35% solution of the salt, and drying first at 175° and finally at 240° in a current of dry air. The material has greater capacity than phosphoric oxide, can be repeatedly reactivated, and does not become sticky on handling or form channels through use.[13]

A salt of univalent manganese, $Na_5Mn(CN)_6$, is precipitated as a microcrystalline powder, very sensitive to oxidising agents, when a solution of sodium manganocyanide is reduced by aluminium and sodium hydroxide, and the resulting solution is filtered into a solution of sodium hydroxide and sodium cyanide saturated with sodium acetate. The potassium salt may be similarly prepared, and variations in the procedure afford similar salts containing a smaller proportion of alkali cyanide. The existence of $K_2Mn(CN)_3$ is highly probable, but if cyanide is used in the final washing of the precipitates the $K_5Mn(CN)_6$ is invariably obtained.[14]

Element No. 75, dvi-manganese or rhenium, the discovery of which was reported in 1925,[15] has been extracted from gadolinite, alvite, columbite, and Norwegian molybdenum glance to the amount of 120 mg. : this has sufficed for a preliminary survey of its chemical and physical properties, which place the element between tungsten and osmium in the Periodic Table.

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[10] F. C. Mathers and H. L. Turner, *Trans. Amer. Electrochem. Soc.*, Sept., 1928, 54; Advance copy; **A.**, 850.

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[12] A. Job and J. Rouvillois, *Compt. rend.*, 1928, **187**, 564; **A.**, 1201.

[13] J. H. Yoe, R. W. McGahey, and W. T. Smith, *Ind. Eng. Chem.*, 1928, **20**, 656; **A.**, 862.

[14] W. Manchot and H. Gall, *Ber.*, 1928, **61**, [*B*], 1135; **A.**, 722.

[15] *Ann. Reports*, 1925, **22**, 63.

Metallic rhenium, obtained by reduction of the sulphide in hydrogen, is a heavy grey powder, unaltered at 2000° in a vacuum: it burns in oxygen at 300°, forming two oxides, Re_2O_7 and ReO_3. The white heptoxide condenses to a colourless liquid which sets to a white solid, m. p. 26—30°, sparingly soluble in water and acids; the less volatile trioxide condenses to a yellow liquid which solidifies to form hygroscopic crystals, m. p. 160°, and, above its boiling point, 450°, yields a vapour from which the heptoxide may be condensed. When reduced by carbon monoxide or sulphur dioxide, these oxides yield green, blue, and violet oxides, which, however, on prolonged heating are reconverted into the yellow or the white oxide. An aqueous solution of the yellow oxide, which is acidic, gives no visible change with hydrochloric, nitric, and sulphuric acids, potassium and sodium hydroxides, ammonia or oxidising agents, but with barium hydroxide and silver nitrate it forms white precipitates, possibly $BaReO_4$ and Ag_2ReO_4, soluble in dilute nitric acid. Hydrogen sulphide is oxidised by the yellow oxide solution with deposition of sulphur, but in the presence of acids a grey sulphide is quantitatively precipitated together with sulphur, and this precipitation is not hindered by oxalic, tartaric, or phosphoric acid (distinction from tungsten). By heating the precipitate in carbon dioxide at 400—600° unstable black sulphides, Re_2S_7 and ReS_3, appear to be formed. Above 600°, the stable black disulphide, ReS_2, is produced. An acidified solution of the yellow oxide will not react with ammonium phosphate or potassium ferrocyanide, nor will it give a colour with potassium xanthate. This behaviour serves to distinguish the element from molybdenum, as do also the behaviour of the solution towards potassium thiocyanate and the greater volatility of rhenium oxide as compared with molybdenum oxide. Absence of any reaction with potassium iodide distinguishes the element from osmium. By heating rhenium in chlorine, two volatile chlorides are formed, $ReCl_6$, brown needles, subliming at 150°, hydrolysed by water; and (?) $ReCl_7$, green, more volatile than the lower chloride. With iodine and bromine vapour, respectively, dark volatile compounds are formed.[16]

Work on the same material by Röntgen spectroscopy has shown a content not exceeding 0·2% of elements lying between copper and uranium, and the *L*-series of rhenium has been thoroughly investigated. Careful examination of the ordinary spectrum indicates that the most persistent lines, especially the triplet at 3640 Å., will serve to detect rhenium down to a concentration of 10^{-7}, and this should greatly facilitate the collection of minerals containing this element.

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[16] W. Noddack, *Z. Elektrochem.*, 1928, **34**, 627; A., 1344.

The metallic powder, *d* 10·4, has been melted in the carbon arc as well as on the anticathode of the Röntgen tube; the metallic beads resemble lead and are stable in air, and their density, obtained by measuring the diameter (0·05 to 0·1 mm.) and weighing on a micro-balance, is about 20. The melting point and boiling point are probably higher than those of tungsten. The specific heat between 0° and 20° is 0·0346, giving by the application of Dulong and Petit's law Re = 185. The exact determination of the equivalent is difficult, as the precise composition of the materials used is uncertain by reason of the ease with which oxidation and reduction take place. The ratio Re : O gave in ReO_3, Re = 189·8, but in Re_2O_7, Re = 196·0, the difference being due in all probability to the readiness with which the heptoxide is converted into the trioxide. Analysis of rhenium hexachloride gave Re = 189·2. The most trustworthy ratio for atomic weight purposes is ReS_2 : Re, which gave as a mean of four determinations Re = 188·71 ± 0·25. This determination is carried out by precipitating rhenium from acid solution as ReS_3 with free sulphur, melting this material with sulphur at 350°, and obtaining Re_2S_7, which by prolonged heating in carbon dioxide at 900° yields the most stable sulphide, ReS_2. The disulphide, heated in hydrogen at 1000°, first forms ReS and is finally completely reduced to the metal.[17]

Group VIII.

Iron pentacarbonyl in appropriate non-aqueous solvents reacts with halogens to give $Fe(CO)_4I_2$, dark brownish-red, $Fe(CO)_4Br_2$, brown, and $Fe(CO)_4Cl_2$, yellow, the last at −20°. These compounds could not be made from ferrous halides and carbon monoxide, into which they are rapidly decomposed by the action of water. The bromide loses carbon monoxide completely in the presence of 2 mols. of pyridine, but under precisely similar conditions the iodide affords the dicarbonyl compound, $Fe(CO)_2I_2,2C_5H_5N$, which loses carbon monoxide completely when treated further with the base. Under the influence of light the chloride is rapidly and completely decomposed, whilst the iodide is less readily affected. The final products of these decompositions are ferrous halides, which are thus readily prepared in the pure state.[18]

A reinvestigation of the composition and properties of ferric sulphide has shown that when the washed precipitate of empirical composition Fe_2S_3 (formed by the addition of ammonium sulphide to a solution of ferric salt, containing tartrate) reacts in neutral solution with mercuric or cadmium salts, it behaves as ferrous or ferric sulphide, respectively. The explanation suggested is that the substance is a mixture of the valency isomerides $S\colon Fe\cdot S\cdot Fe\colon S$ and FeS,FeS_2.[19] The dependence of the composition of the sulphide on conditions of precipitation previously worked out [20] is also valid for the mercaptides of iron, for whilst ordinary solutions of ferric salts give ferrous mercaptide with ethyl mercaptan, if the concentration of ferric iron is depressed by the addition of tartrate, ferric ethyl mercaptide results.

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[17] (Frau) I. Noddack, *Z. Elektrochem.*, 1928, **34**, 629.

[18] W. Hieber and G. Bader, *Ber.*, 1928, **61**, [*B*], 1717; **A.**, 1202.

Ferric sulphide has been shown to be the principal product of the reaction of ferric hydroxide with hydrogen sulphide at 100°; the mono- and di-sulphides also present are believed to result from the partial decomposition of this compound.[21]

Considerations of space preclude even reference to a great deal of interesting work done on the preparation of co-ordination and other compounds of the metals of this group.

Iridium hexa- and penta-fluorides have been prepared by the passage of pure fluorine over the metal heated in a boat of calcined fluorspar supported in a tube of the same material heated electrically. Vessels of fluorspar calcined at 1280°, which are readily worked mechanically by means of an emery wheel, are resistant to fluorine at high temperatures.[22]

The formation of a volatile platinum carbonyl chloride when carbon monoxide is passed over heated platinum chloride has been applied in the separation of platinum from kindred metals. The platinum carbonyl chloride decomposes at about 300° with the formation of platinum, carbon monoxide, chlorine, and carbonyl chloride, and the metal may be recovered in a compact form on a platinum wire heated at about 600° in the vapour of the compound.[23]

Systems and Equilibria.

A great deal of work has been done on various types of systems and equilibria which it is impossible to describe in this Report. It may be useful, however, to give here the titles in the order in which they appear in the Abstracts.

Barium bromide–radium bromide–hydrogen bromide–water [24]; cuprous chloride–cupric chloride [25]; sodium carbonate–sodium hydrogen carbonate–water[26]; ferric nitrate–potassium nitrate–water[27]; manganese sulphate–potassium sulphate–water; manganese sulphate–ammonium sulphate–water; copper sulphate–sodium sulphate–water[28]; sodium oxide–arsenic oxide–water[29]; magnesium sulphate–water[30]; ethyl alcohol–carbon tetrachloride[31]; aluminium nitrate–potassium nitrate–ferric nitrate–water[32]; iron–copper–sulphur[33]; copper sulphate–sodium sulphate–water[34]; sodium oxide–nitrogen pentoxide–water[35]; potassium carbonate–sodium carbonate–water[36]; mercuric iodide–potassium iodide–water[37]; ferrous chloride–nickel chloride–water[38]; manganous phosphate–phosphoric acid–water[39]; water–sodium chloride–magnesium sulphate–magnesium chloride–sodium sulphate[40]; water–sodium nitrate–sodium chloride–sodium sulphate[41]; aluminium chloride–potassium chloride–hydrogen chloride–water[42]; ferric chloride–aluminium chloride–water[43]; thorium oxide–carbon[44]; aluminium oxide–carbon[45]; ammonium dichromate–potassium sulphate–potassium chloride; ammonium dichromate–iron–sulphur[46]; thallium–phosphorus[47]; potassium oxalate–water[48];

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[22] O. Ruff and J. Fischer, *Z. Elektrochem.*, 1927, **33**, 560; **A.**, 1928, 382.

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[25] W. Biltz and W. Fischer, *ibid.*, p. 290; **A.**, 1927, 1141.

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[44] C. H. Prescott, jun., and W. B. Hincke, *J. Amer. Chem. Soc.*, 1927, **49**, 2744; **A.**, 1928, 20.

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[14] (Signa.) E. Fabris, *Ann. Chim. Appl.*, 1928, **18**, 326; **A.**, 1095.

[15] E. Jänecke, *Z. angew. Chem.*, 1928, **41**, 916; **A.**, 1095.

[16] W. C. Hansen, *J. Amer. Chem. Soc.*, 1928, **50**, 2155; **A.**, 1095.

[17] J. R. Baylis, *J. Physical Chem.*, 1928, **32**, 1236; **A.**, 1095.

[18] K. Matsuyama, *Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 783; **A.**, 1095.

[19] E. Abel, O. Redlich, and J. Adler, *Z. anorg. Chem.*, 1928, **174**, 257; **A.**, 1190.

[20] K. Jellinek and A. Rudat, *ibid.*, **175**, 281; **A.**, 1191.

[21] E. Abel, O. Redlich, and J. Adler, *ibid.*, **174**, 269; **A.**, 1191.

[22] R. M. Caven and W. Johnston, *J.*, 1928, 2506; **A.**, 1191.

[23] M. de K. Thompson, *Trans. Amer. Electrochem. Soc.*, Sept. 1928, Advance copy; **A.**, 1191.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

Hydrocarbons.

A CONSIDERABLE number of papers dealing with the chemistry of the aliphatic hydrocarbons has appeared during the past few years and the position now reached would appear to warrant the inclusion of this section in the present Report.

Studies of the complex decompositions undergone by simple hydrocarbons under the influence of heat have revealed that in silica vessels, which possess no appreciable catalytic activity, ethane at 575° yields only ethylene and hydrogen. Further reactions between ethylene and hydrogen then take place, accompanied by the polymerisation of ethylene and the formation of higher hydrocarbons, propylene, methane, and ethane. It is probable that surface action plays a prominent part in bringing about the changes. With propane under the same conditions the following three reactions appear to take place, (*a*) and (*b*) being rapid and (*c*) slow :

$$(a)\ C_3H_8 \longrightarrow C_2H_4 + CH_4 \qquad (b)\ C_3H_8 \longrightarrow C_3H_6 + H_2$$
$$(c)\ 2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4.$$

At lower temperatures (200—400°) in the presence of a nickel catalyst a different course is followed :

$$(a)\ C_3H_8 \longrightarrow 2CH_4 + C$$
$$(b)\ C_3H_8 \longrightarrow C_3H_6 + H_2 \longrightarrow CH_4 + 2H_2 + C.$$

The latter reaction becomes prominent only at the higher temperatures. Under these conditions hydrogen is without effect on the decomposition but the nature of the catalyst is of great importance.[1]

The rate of dissociation of the simpler hydrocarbons in Pyrex glass tubes at 650° under 1 atmosphere pressure has been shown to depend on the comparative complexity of the molecule, the main reactions in the cases of ethane, propane, *n*- and *iso*-butane being, under the prescribed conditions, dehydrogenation and demethanation.[2]

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[1] F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, 1928, **20**, 948; **A.**, 1211.

When a mixture of hydrogen and ethylene is exposed to ultraviolet light in the presence of mercury vapour, the hydrocarbons methane, ethane, propane, and butane are produced. Under similar conditions ethane is unaffected, and the authors [3] consider that the results can be explained most readily by postulating the intermediate formation of atomic hydrogen, methylene by fission of the ethylene, and ethylene activated by loss of hydrogen.

Another example of the complex nature of the rearrangements observed during reactions of this type is to be found in the changes undergone by propyl alcohol when it is passed over uranium oxide at 400°. The reaction products include propaldehyde, β-methylpentenal and αβ-dimethyl-$\Delta^{\alpha\beta}$-heptadienal and, by further decomposition of these substances, hydrogen, methane, unsaturated hydrocarbons, hexane, hexene, and carbon monoxide and dioxide.[4]

The polymerisation of acetylene under the influence of heat has been studied with a variety of catalysts and at different temperatures. The maximum yield of polymerised product (82%) was obtained by passing a slow stream of the gas over clay in a glass tube heated at 650°, and in this case the resulting tar by fractional distillation yielded mainly benzene, naphthalene, and other aromatic hydrocarbons. In a metal tube decomposition of the acetylene into carbon, hydrogen, and other gaseous substances took place more readily than polymerisation and the composition of the polymerised material was different, little or no naphthalene being present.[5]

An instance of the usefulness of high-temperature reactions as a means of obtaining acetylenic hydrocarbons is to be found in the dehalogenation of αα-dichloroheptane by passage of its vapour over soda-lime at 420°, the corresponding acetylene, $C_5H_{11}\cdot C{:}CH$, being obtained in a yield of 10%.[6]

Acetylene and carbon dioxide react when heated together in the presence of metallic catalysts to give saturated hydrocarbons, a smaller amount of unsaturated hydrocarbons, carbon monoxide, and water. Acetylene–carbon monoxide mixtures, with nickel and cobalt as catalysts, give various aldehydes (formaldehyde, acetaldehyde, acraldehyde) and a mixture of unsaturated hydrocarbons of high molecular weight, along with carbon dioxide and water.[7]

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[2] R. N. Pease, *J. Amer. Chem. Soc.*, 1928, **50**, 1779; **A.**, 988.

[3] A. R. Olson and C. H. Meyers, *ibid.*, 1927, **49**, 3131; **A.**, 1928, 150.

[4] A. Mailhe and Renaudie, *Compt. rend.*, 1928, **186**, 238; **A.**, 268.

[5] C. Fujio, *J. Soc. Chem. Ind. Japan*, 1928, **31**, 77; **A.**, 732.

[6] C. Sandonnini, *Gazzetta*, 1927, **57**, 781; **A.**, 1928, 43.

[7] A. J. Hill and F. Tyson, *J. Amer. Chem. Soc.*, 1928, **50**, 172; **A.**, 269.

Amongst other reactions of a similar nature which have been recorded there may be mentioned the polymerisation and depolymerisation of amylenes under the influence of heated silicates, where again a complex mixture results containing butylene, heptylene, octylene, nonylene, *iso*pentane, and other products, both saturated and unsaturated.[8]

The action of the silent electric discharge on ethylenic hydrocarbons appears to be closely similar to that of high temperature and pressure, prolonged action resulting in the production of highly polymerised non-volatile substances. The rate of the reaction is greatly dependent upon the structure of the original hydrocarbon and only slightly on the amount of the electric tension. In the case of *iso*butylene polymerisation is accompanied by a redistribution of hydrogen atoms, and on fractional distillation of the product mainly saturated hydrocarbons are found in the portions of lower boiling point. Fission of the carbon chain and re-arrangement of alkyl groups leading to the formation of hydrocarbons containing highly branched structures are marked features of the reaction. Naphthenes, but no aromatic substances, are found amongst the fractions of higher boiling point.[9]

An extensive contribution to the chemistry of the allene hydrocarbons and their derivatives has been made by N. Bouis,[10] who employs the appropriately substituted allyl alcohol, $R{\cdot}CH(OH){\cdot}CH{:}CH_2$, as starting point in the preparation of the hydrocarbons. The action of phosphorus tribromide on these alcohols is accompanied by isomerisation and leads exclusively to the formation of $R{\cdot}CH{:}CH{\cdot}CH_2Br$.[11] Addition of bromine at 0° now gives the tribromide, $R{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$, which when fused with 75—80% potassium hydroxide yields the allene dibromide, $R{\cdot}CHBr{\cdot}CBr{:}CH_2$, from which the allene, $R{\cdot}CH{:}C{:}CH_2$, is prepared by dropwise addition of the dibromide to zinc dust in boiling alcohol. For a detailed description of the various allenes and of the numerous intermediate products and their derivatives the reader is referred to the original paper. The addition of bromine (1 mol.) occurs mainly at the $\beta\gamma$-positions, the $\alpha\beta\beta\gamma$-tetrabromo-derivative resulting from the addition of a second molecule of bromine. Treatment of the allene hydrocarbons with concentrated sulphuric acid at —10°, followed by the action of water, gives rise to the ketone $CH_2R{\cdot}CO{\cdot}CH_3$, and sodamide reacts with the allenes to form sodium derivatives of the isomeric acetylenes, $CH_2R{\cdot}C{:}CNa$.

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[8] S. V. Lebedev and I. A. Vinogradov-Volzynski, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 441; **A.**, 732.

[9] N. D. Prianischnikov, *Ber.*, 1928, **61**, [*B*], 1358; **A.**, 866.

[10] *Ann. Chim.*, 1928, [x], **9**, 402; **A.**, 1112.

[11] See H. Burton and C. K. Ingold, *J.*, 1928, 904; **A.**, 634.

Much attention is being devoted to the properties of hydrocarbons possessing conjugated double bonds and it is desirable to review in somewhat greater detail certain of the more important papers which have appeared in this connexion. Derivatives of $\beta\gamma$-dimethylbutadiene and of tetramethylbutadiene have been studied by A. D. Macallum and G. S. Whitby,[12] who find that the former of these substances yields two dibromides, one solid and one liquid. The solid is highly reactive and is shown by ozonolysis to be a 1 : 4-dibromo-compound. Some evidence is given in favour of the view that the solid and liquid dibromides possess respectively *trans*- and *cis*-configurations. The same authors reach the conclusion that, in general, butadienes substituted in positions 1 and 4 polymerise less readily than the corresponding 2 : 3-derivatives, thus confirming the views of earlier workers.[13]

Results of great interest are described in a paper dealing with the bromine addition compounds derivable from butadiene.[14] It has long been known that under certain specified conditions the principal product which can be isolated is the solid 1 : 4-dibromide [15] and it has been generally assumed that the addition gives exclusively the 1 : 4-product. It now appears that the isomeric 1 : 2-dibromide is invariably formed during the reaction and that this is an unstable substance which undergoes slow spontaneous conversion into the 1 : 4-isomeride. It does not follow, however, in view of the experimental evidence now obtained, that the reaction can be adequately explained on the basis of 1 : 2-addition, followed by isomerisation. Another view would seek to account for the formation of the two products by considering that the hydrocarbon is capable of assuming different polarised forms, $C-C-\overset{+}{C}-\overset{-}{C}$ and $\overset{+}{C}-C-C-\overset{-}{C}-$. A third possibility, also suggested in the communication now under review, is to regard the observed result as incidental to the operations involved in the addition process. According to this idea the first stage of the reaction is of the normal ethylenic type and involves the formation of an addition complex of butadiene and molecular bromine. This is represented by the novel electronic formula (I). Its existence is transient and the subsequent events lead either to the formation of the 1 : 2-dibromide (II) (normal course), or to the 1 : 4-dibromide (III), if the tautomeric properties of the propene system $CBr\cdot C{:}C \rightleftharpoons C{:}C\cdot CBr$ are brought into play. The mechanism involved is illustrated by the accompanying electronic formulæ.

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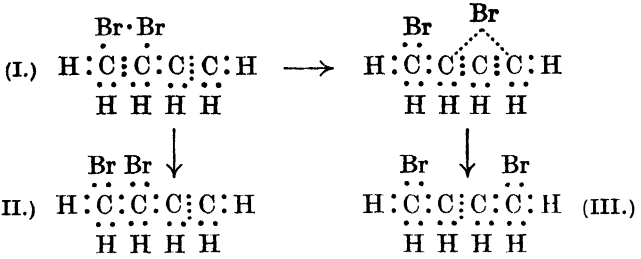
[12] *Trans. Roy. Soc. Canada*, 1928, [iii], **22**, 33, 39; **A.**, 614.

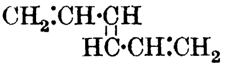
[13] S. V. Lebedev and B. K. Mereshkovski, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249; *A.*, 1913, i, 1285.

[14] E. H. Farmer, C. D. Lawrence, and J. F. Thorpe, *J.*, 1928, 729; **A.**, 504.

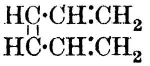
[15] G. Griner, *Compt. rend.*, 1893, **116**, 723; **117**, 553; *A.*, 1893, i, 450; 1894, i, 62; J. Thiele, *Annalen*, 1899, **308**, 333; *A.*, 1900, i, 2.



The additive properties of the conjugated system in hexatriene have also been studied.[16] Two forms of the parent hydrocarbon have been found to exist, these being represented respectively as *cis*- and *trans*-isomerides,

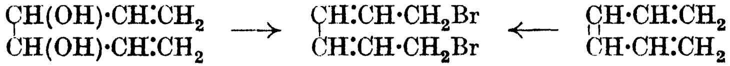


$$\begin{array}{l} CH_2{:}CH{\cdot}CH \\ \qquad\qquad \| \\ \qquad\qquad HC{\cdot}CH{:}CH_2 \end{array}$$



$$\begin{array}{l} HC{\cdot}CH{:}CH_2 \\ \| \\ HC{\cdot}CH{:}CH_2 \end{array}$$

It has been established that the 3 : 4 glycol (I), which has been shown to exist in two stereoisomeric forms, gives on bromination both the 3 : 4- and the 1 : 6-dibromide (II) and that the hexatriene (III) derived from the latter also adds bromine terminally. Migration of bromine would appear to be involved in the 3 : 4-glycol ⟶ 1 : 6-dibromide transformation, an observation which, if found to be general, will be of considerable importance in arriving at views concerning the reactive forms of conjugated hydrocarbons,



$$\begin{array}{ccccc} \begin{array}{l} CH(OH){\cdot}CH{:}CH_2 \\ | \\ CH(OH){\cdot}CH{:}CH_2 \end{array} & \longrightarrow & \begin{array}{l} CH{:}CH{\cdot}CH_2Br \\ | \\ CH{:}CH{\cdot}CH_2Br \end{array} & \longleftarrow & \begin{array}{l} CH{\cdot}CH{:}CH_2 \\ \| \\ CH{\cdot}CH{:}CH_2 \end{array} \\ \text{(I.)} & & \text{(II.)} & & \text{(III.)} \end{array}$$

When addition of bromine occurs in the absence of hydrogen bromide, both the *cis*- and the *trans*-form of hexatriene yield 1 : 2-dibromides. These 1 : 2-dibromides are convertible into the 1 : 6-forms, which are obtained, directly, as mentioned above, by the use of ordinary commercial bromine containing traces of hydrogen bromide. It is possible, therefore, to consider the chemistry of hexatriene on the basis of bromine-migration reactions, but the authors do not rule out altogether the possibility of direct 1 : 6-addition, which could be explained by assuming suitable polarisation of the conjugated molecule in the sense demanded by the modern extension of the Thiele hypothesis.

Investigations of the additive properties of butadiene derivatives have also been carried out by C. Prévost,[17] who interprets the experimental results by means of the bromine-migration hypothesis, and considers that the 1 : 4- and 1 : 2- (or 3 : 4)-forms of the semi-saturated derivatives are tautomeric. In the case of butadiene, if the sole primary addition product is the 1 : 2-compound, then changes in experimental conditions affecting the 1 : 2 $\rightleftharpoons$ 1 : 4 isomerisation should have a corresponding effect on the proportion of the two isomerides found in the bromination mixture. Actually the rate of isomerisation is found [18] to be little affected by experimental conditions and is much too slow to account for the large percentages of 1 : 4-derivative which are observed. On the other hand, these percentages are much influenced by the nature of the solvent employed, and it was for these reasons that the alternative hypothesis just outlined was put forward by Farmer, Lawrence, and Thorpe.

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[16] E. H. Farmer, B. D. Laroia, T. M. Switz, and J. F. Thorpe, *J.*, 1927, 2937; **A.**, 1928, 151.

The properties of conjugated systems are being investigated also by a study of their behaviour during catalytic hydrogenation in the presence of platinum-black.[19] Four types of process are theoretically possible according to the order in which the conjugated double bonds become saturated. The first considered is one which proceeds in accordance with Thiele's rule, where primary addition of hydrogen is exclusively in positions 1 and 4, followed by hydrogenation at a different rate of the ethylenic derivative so produced. Substances such as di*iso*butenyl, $CMe_2{:}CH{\cdot}CH{:}CMe_2$, in which all the four hydrogen atoms in the 1 : 4 positions are replaced by aliphatic radicals, belong to this group. The second type is more complex and does not follow Thiele's rule. The addition of hydrogen takes place in all the possible directions, 1 : 2, 3 : 4, and 1 : 4, and is further complicated by the simultaneous formation of fully saturated molecules. Isoprene, for example, by the addition of 1 mol. proportion of hydrogen yields *iso*pentane (30%), *iso*propylethylene (12%), *as*-methylethylethylene (13%), trimethylethylene (15%), and unchanged isoprene (30%). Divinyl, piperylene, and di*iso*propenyl also belong to this type.

The simultaneous addition of two molecules of hydrogen, with the formation of a fully saturated substance, was suggested by C. Paal [20] as the normal method of hydrogenation of conjugated compounds. This, however, (Lebedev's Type III) has not yet been observed experimentally and a further investigation of the cases described by Paal reveals that they do not in fact belong to this type.

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[17] *Compt. rend.*, 1926, **183**, 1292; **A.**, 1927, 131; 1927, **184**, 1460; **A.**, 1927, 748; 1928, **186**, 1209; **A.**, 613; *Bull. Soc. chim.*, 1928, [iv], **43**, 996; **A.**, 1212.

[18] E. H. Farmer, C. D. Lawrence and J. F. Thorpe, *loc. cit.*

[19] S. V. Lebedev and A. O. Yakubchik, *J.*, 1928, 823, 2190; *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 981; **A.**, 1928, 613, 1111.

[20] *Ber.*, 1912, **45**, 2221; *A.*, 1912, i, 703.

The classification is completed by consideration of a fourth type in which addition of hydrogen occurs exclusively in the 1 : 2- and 3 : 4-positions, no 1 : 4-addition products being formed. Here again the process does not follow Thiele's rule. In all cases when one molecule of hydrogen has been added the number of unchanged (conjugated) molecules is equal to the number of fully saturated molecules. A characteristic point during the hydrogenation, and one which determines fully the course of the reaction, is reached when the whole of the original conjugated system is consumed. The authors term this the "critical point of hydrogenation of a conjugated system."

In this connexion it is of interest to refer to some hydrogenation experiments performed with the aid of sodium amalgam.[21] The preparation of pure amalgam is described and this is found to differ widely in properties from that prepared in the usual way. For example, according to von Baeyer, terephthalic acid is reduced exclusively to $\Delta^{2:5}$-dihydroterephthalic acid, which does not undergo further hydrogenation. Under similar conditions with pure amalgam, Δ^2-tetrahydrophthalic acid is formed, and, contrary both to the hitherto accepted evidence and to the postulates of Thiele's theory, the Δ^2-tetrahydrophthalic acid hydrogenates much more rapidly than the corresponding Δ^1-acid. The isomerising influence of the alkali hydroxide exerted for very different lengths of time may possibly help to explain the observed differences.

Consideration of the mechanism of these reductions indicates that the evolution of nascent hydrogen, which is then added at the double bond of the organic molecule, must be regarded as highly improbable, and instead of this the addition of sodium at the double linking is postulated, the resulting product being afterwards decomposed by the water present.[22]

These views may be compared with those advanced by A. Gillet [23] in interpreting the hydrogenation of conjugated compounds. This author regards the process as due to the addition of two sodium atoms in the 1 : 2-positions followed by isomerisation: $>CNa{\cdot}CHNa{\cdot}CH{:}C< \longrightarrow >CNa{\cdot}CNa{:}CH{\cdot}CH<$. In a more recent paper [24] this interpretation is objected to on the ground that it affords no explanation of the hydrogenation of conjugated compounds by agents, other than sodium, which act by virtue of the production of nascent hydrogen.

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[21] R. Willstätter, F. Seitz, and E. Bumm, *Ber.*, 1928, **61**, [*B*], 871; **A.**, 756.

[22] Compare W. Schlenk and E. Bergmann, *Annalen*, 1928, **463**, i; **A.**, 1031; this Report, p. 96.

[23] *Bull. Soc. chim.*, 1927, [iv], **41**, 927; **A.**, 1927, 921.

[24] G. Vavon, *ibid.*, p. 1598; **A.**, 1928, 150.

Aldehydes and Ketones.

The fact that the β-hydroxypropane-β-sulphonic acid obtained by hydrolysis of phenyl propane-ββ-disulphonate is not identical with " acetone bisulphite "[25] is at variance with the views of F. Raschig and W. Prahl on the structure of the bisulphite addition compounds.[26] The experiments with phenyl propane-ββ-disulphonate have therefore been repeated by the latter authors, who have failed to confirm Schroeter's results and maintain their formulation of the bisulphite addition compounds as hydroxy-sulphonic acids, $R_2C(OH)(SO_3H)$.[27] In a vigorous reply by Schroeter new evidence is given in support of his original observations. Since the bisulphite compounds cannot be regarded as sulphurous esters, and Schroeter regards the hydroxy-sulphonic acid structure as disproved, a unitary formulation becomes impossible and the structure $(R_2C{:}O)(SO_2)(HOH)$ is now postulated. In this the known labile additive compound of the aldehyde or ketone with sulphur dioxide is regarded as uniting with water to give a more stable substance, which can behave as a monobasic acid.[28] On the other hand, the strong evidence adduced by Raschig and Prahl in favour of the hydroxy-sulphonic acid structure has been supplemented and confirmed by studies of the Röntgen-ray and absorption spectra of such substances.[29]

The preparation of aldehydes by Rosenmund's method has been found to proceed more rapidly when freshly precipitated barium sulphate is used in preparing the palladium catalyst, and the availability of the method is exemplified in the reduction of stearyl chloride. In this case the stearaldehyde produced is accompanied by a solid dimeride, $(C_{18}H_{36}O)_2$, which possesses no aldehydic properties but yields stearaldehyde on distillation under diminished pressure.[30]

A comparison of the reactivities of various alcohols for acetal formation has been made by a study of the rates of reaction of acetaldehyde with methyl, ethyl, *iso*propyl, and *n*-butyl alcohols, specially purified materials being used in the presence of a trace of hydrogen chloride. The water eliminated is shown to have a marked effect on the progress of the reaction, the hemi-acetal first formed undergoing hydrolysis, with the result that the apparent value of the bimolecular coefficient for the reaction between the hemi-acetal and the alcohol diminishes with time. The four alcohols show only slight differences in behaviour.[31] The converse problem, involving the relation of the structure of ketones to their reactivity in acetal formation, has also been investigated.[32] In this case the extent of acetal formation between ethyl orthoformate and various ketones was measured by a specially devised analytical method. Of the following eight ketones—acetone, methyl ethyl, diethyl, methyl *n*-hexyl, methyl *tert.*-butyl ketones, acetophenone, propiophenone, and benzophenone—acetone showed most reactivity (90% acetal formation) and methyl *tert.*-butyl ketone least (12%). In general, substitution of higher *n*-alkyl radicals for the methyl group in acetone reduces the reactivity slightly, greater reductions being observed with the aromatic ketones.

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[25] G. Schroeter, *Ber.*, 1926, **59**, [*B*], 2341; **A.**, 1926, 1226.

[26] F. Raschig and W. Prahl, *Annalen*, 1926, **448**, 265; **A.**, 1926, 939. See *Ann. Reports*, 1927, **24**, 66.

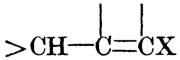
[27] *Idem*, *Ber.*, 1928, **61**, [*B*], 179; **A.**, 273.

[28] G. Schroeter (with M. Sulzbacher), *ibid.*, p. 1616; **A.**, 1216.

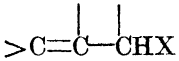
[29] O. Stelling, " Zusammenhang zwischen Chemischer Konstitution und K-Röntgen-Absorptions Spektra," Lund, 1927, p. 168; *Cellulose Chem.*, 1928, **9**, 100; **A.**, 1217.

[30] R. Feulgen and M. Behrens, *Z. physiol. Chem.*, 1928, **177**, 221; **A.**, 1117.

Compounds possessing the general skeleton (I) or (II), where X is an electro-negative group, are usually tautomeric, the mobility and point of equilibrium being the resultant of structural factors.

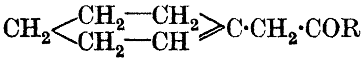
(I.) 

$>CH-\overset{|}{C}=\overset{|}{C}X$

 (II.)

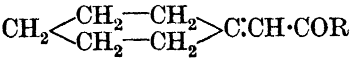
$>C=\overset{|}{C}-\overset{|}{C}HX$

Investigations into the properties of such systems have now been extended to include *cyclo*hexylideneacetone and *cyclo*hexylidene-methyl ethyl ketone.[33] Each of these substances reacts in two forms, (III) and (IV), both of which have been isolated. These show



$CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH\end{matrix}>C\cdot CH_2\cdot COR$

(III.)



$CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>C:CH\cdot COR$

(IV.)

characteristic differences in physical and chemical properties, and under the influence of catalysts each form undergoes partial conversion into the other, the equilibrium mixture containing about 70% of (IV). It was found that the freshly formed *cyclo*hexylidene-acetone is much more labile than the purified material and it is suggested that the greatly enhanced reactivity is to be attributed to the changed properties of substances *in statu nascendi*.[34] The proof thus supplied of the existence of pairs of substances which form an equilibrium mixture under the influence of catalysts emphasises the analogy existing between tautomeric substances of the keto-enol class and those containing the "three-carbon system." Further evidence in this connexion is being obtained from a study of the condensation of ketones with ethyl acetoacetate to give tautomeric substances of such a type as

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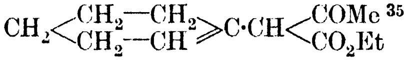
[31] H. Adkins and A. E. Broderick, *J. Amer. Chem. Soc.*, 1928, **50**, 178; **A.**, 274.

[32] H. E. Carswell and H. Adkins, *ibid.*, p. 235; **A.**, 274.

[33] A. H. Dickins, W. E. Hugh, and G. A. R. Kon, *J.*, 1928, 1630; **A.**, 887.

[34] Compare F. R. Goss and C. K. Ingold, *J.*, 1925, **127**, 2776; **A.**, 1926, 289.

(V.) 

$$CH_2{<}\genfrac{}{}{0pt}{}{CH_2-CH_2}{CH_2-CH}{>}C\cdot CH{<}\genfrac{}{}{0pt}{}{COMe}{CO_2Et}$$ [35]

A more complicated system containing the three-carbon skeleton is found amongst the substances obtained by the catalytic intermolecular condensation of methyl ethyl ketone. The four products theoretically probable may be divided into two pairs (I) and (II), (III) and (IV), each pair consisting of substances which should

(I.) $CH_2Me\cdot CMe\colon CH\cdot COEt$ $CHMe\colon CMe\cdot CH_2\cdot COEt$. (II.)
(III.) $CH_2Me\cdot CMe\colon CMe\cdot COMe$ $CHMe\colon CMe\cdot CHMe\cdot COMe$. (IV.)

exhibit tautomerism of the type now under consideration. As the result of recent work in this difficult field all the above four substances have been synthesised and the relationships existing between the various homomesitones have been successfully established.[36] It appears that alkaline condensing agents acting on methyl ethyl ketone lead to mixtures of (I) and (II) containing the former in excess. Acid condensing agents, on the other hand, give ketones with a branched chain, (III) and (IV), sulphuric acid giving mainly (IV) and hydrochloric acid (III). Definite indications have been obtained that the homomesitones display *cis-trans* isomerism; for example, (IV) gives two different semicarbazones, m. p. 203—204° and 163°. It has also been proved that the homomesitones exhibit tautomerism of the expected kind. For instance, (I) or (II) under the influence of catalysts yields an equilibrium mixture which contains some 68% of the $\alpha\beta$-compound. In this case the mobility is high, but with (III) and (IV) a very low mobility is encountered and the final equilibrium mixture contains only 17% of the $\alpha\beta$-compound. The difference between the two pairs of ketones is probably attributable to the effect produced by the α-methyl group in (III) and (IV), which has already been found to favour the $\beta\gamma$-phase in certain cases.[37]

The catalytic condensation of methyl ethyl ketone has been examined also by A. Petrov,[38] who finds that, at the ordinary temperature and under the influence of agents such as hydrogen chloride, sulphuric acid and sodium ethoxide, products analogous to those derivable from acetone are obtained, but that the yield of triethylbenzene is remarkably small. At about 400°/100 atm., in the presence of aluminium oxide, the total yield of hydrocarbons from methyl ethyl ketone is very low (8%), homomesitylene oxide and homo*iso*phorone being obtained. The action of sodamide at 0° results in the formation of a mixture containing the four possible homo*iso*phorones, $C_{12}H_{20}O$, but the isomerides (A) and (B) seem to predominate :

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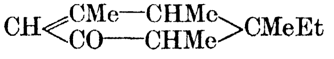
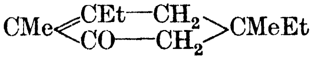
[35] L. G. Jupp, G. A. R. Kon, and E. H. Lockton, *J.*, 1928, 1638; **A.**, 885.

[36] (Miss) A. E. Abbott, G. A. R. Kon, and R. D. Satchell, *ibid.*, p. 2514; **A.**, 1218.

[37] See G. A. R. Kon and B. T. Narayanan, *J.*, 1927, 1536; **A.**, 1927, 873; A. A. Goldberg and R. P. Linstead, *J.*, 1928, 2343; **A.**, 1214.

(A) 

$\mathrm{CH}<\begin{matrix}\mathrm{CMe{-}CHMe}\\ \mathrm{CO{-}CHMe}\end{matrix}>\mathrm{CMeEt}$

 (B)

$\mathrm{CMe}<\begin{matrix}\mathrm{CEt{-}CH_2}\\ \mathrm{CO{-}CH_2}\end{matrix}>\mathrm{CMeEt}$

Acids.

Differences of opinion continue to exist concerning the mechanism of Kolbe's electro-synthesis of hydrocarbons. The view of Schall,[39] that acid peroxides are the intermediate products formed at the anode during the electrolysis of fatty acids, has been strongly supported by the work of F. Fichter,[40] who extends the peroxide theory to electro-chemical oxidation in general. Direct evidence in support of the peroxide theory is claimed as the result of experiments with potassium hexoate, which, when electrolysed at low temperatures, was found to yield small quantities of the acid peroxide. From a comparison of the course of decomposition of the peroxide and the per-acid with the behaviour of the acid during electrolysis it appeared that the latter reaction proceeded *via* the peroxide.

On the other hand, O. J. Walker [41] has obtained evidence which is regarded as incompatible with the peroxide theory. This author holds that the detection of peroxides during electrolysis furnishes no proof that the Kolbe reaction itself proceeds through these intermediate compounds, and comments are made on the great difficulties encountered in isolating from the electro-chemical products any peroxide, even at temperatures where the peroxide is known to be stable. Furthermore, a study of the thermal decomposition of acetyl peroxide, in the pure state or in solution, shows that only small amounts of ethane are produced, although comparatively large quantities of methane are formed. Since methane is never found amongst the anode gases during the electrolysis of acetates, whereas ethane is still formed at temperatures (100°) far above the decomposition point of acetyl peroxide, the available experimental evidence is held to be decidedly against the peroxide theory.

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[38] *Ber.*, 1927, **60**, [*B*], 2548; **A.**, 1928, 156.

[39] *Z. Elektrochem.*, 1896, **3**, 83; *A.*, 1897, i, 317.

[40] *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 131; *A.*, 1924, i, 629; *J. Chim. physique*, 1926, **23**, 481; **A.**, 1926, 912; F. Fichter and R. Zumbrunn, *Helv. Chim. Acta*, 1927, **10**, 869; **A.**, 1928, 45.

[41] *J.*, 1928, 2040; **A.**, 1114.

Treatment of a solution of oxalic acid at 60° with a deficiency of potassium permanganate in an inert atmosphere results in the formation of an activated variety of oxalic acid, which in nearly neutral solution is capable of reducing chromic acid, bromine, bromate, and nitrate, as well as salts of silver, platinum, and mercury. The activated form was not isolated and yielded quantitatively the ordinary calcium oxalate. The activated acid regained its normal properties slowly at the ordinary temperature and more rapidly when heated.[42]

A study of the action of thionyl chloride on organic acids reveals surprising differences from acid to acid. For example, oxalic, tartaric, and fumaric acids are unattacked, chloroacetic acid (but not trichloroacetic acid or glycine), malonic, suberic, and sebacic acids form acid chlorides, and succinic, glutaric, and maleic acids yield anhydrides. In the aromatic series, acid chloride formation is more general, but here again certain acids (*e.g.*, terephthalic and *p*-hydroxybenzoic) remain unaffected and others (phthalic acid) give the anhydride.[43]

It has been found that the action of acetic anhydride on simple monocarboxylic acids yields only the simple acid anhydride and not a mixed anhydride as is generally supposed. The simple anhydride often crystallises with one molecule of acetic anhydride of crystallisation, giving a substance whose empirical formula is identical with that of the mixed anhydride.[44]

The action of bromine water on olefinic acids has been investigated from the point of view of the effect of the concentration of the acid.[45] By maleic acid in 0·05*N*-aqueous solution 89·3% of the reacting bromine was converted into the bromohydrin, and this proportion fell to 62·5% in a 0·33*N*-solution. Maleic acid therefore behaves similarly to ethylene and allyl alcohol.[46] Sodium maleate reacts much more rapidly than the free acid with increase in the proportion of bromohydrin (95·6% at 0·05N: 75·6% at 0·33N). Under similar conditions, fumaric acid reacted with extreme slowness, and the sodium salt gave, with a velocity about half that of the maleate, a slightly enhanced proportion of bromohydrin. With oleic acid (0·1N-mixture), only some 51% of the bromine was found to be effective. Although it was formerly considered essential to carry out experiments of this type at a low temperature and in the absence of bright light, it is now known that in certain cases light promotes the reaction; and it is shown that with oleic acid, raising the temperature to 90° results in increased yields of the bromohydrin.

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[42] F. Oberhauser and W. Hensinger, *Ber.*, 1928, **61**, [*B*], 521; **A.**, 505; A. E. Tschitschibabin, *J. pr. Chem.*, 1928, **120**, 214; **A.**, 1929, 48.

[43] L. McMaster and F. F. Ahmann, *J. Amer. Chem. Soc.*, 1928, **50**, 145; **A.**, 271.

[44] A. W. Van der Haar, *Rec. trav. chim.*, 1928, **47**, 321; **A.**, 393. Contrast W. Autenrieth, *Ber.*, 1887, **20**, 3187; *A.*, 1888, 250, and P. Askenasy and V. Meyer, *Ber.*, 1893, **26**, 1354; *A.*, 1893, 507.

[45] J. Read and W. G. Reid, *J.*, 1928, 745; **A.**, 505. Compare E. Biilmann, *Rec. trav. chim.*, 1917, **36**, 313; *A.*, 1917, i, 378.

[46] J. Read and R. G. Hook, *J.*, 1920, **117**, 1214; J. Read and E. Hurst, *J.*, 1922, **121**, 989.

A comparison of the behaviour of acid anhydrides and of acids when passed over heated thoria, shows that the former are converted more easily into the corresponding ketones; and it is suggested that, in the synthesis from acids, ketones arise rather from the intermediate formation and decomposition of the anhydrides than through the thorium salts. Experiments on the formation of acetic anhydride from acetic acid by passage over titanic oxide at 300° are described in support of this view.[47]

The catalytic decomposition of suberic acid under the influence of heat is found to proceed most satisfactorily in the presence of an equal weight of iron filings along with 5% by weight of crystallised baryta. Yields up to 40% of suberone are thus obtainable. In this case also, the mechanism of reaction which is considered most probable involves the intermediate formation of the acid anhydride.[48]

A continuation of researches on the action of heat on salts of polymethylenedicarboxylic acids, the earlier stages of which have already received mention in these Reports,[49] has now led to the formation of rings containing as many as twenty-two carbon atoms. For instance, the action of heat on the yttrium salt of nonane-1 : 9-dicarboxylic acid furnishes some *cyclo*eicosane-1 : 11-dione, which, when reduced by Clemmensen's method, yields *cyclo*eicosanone. The same cyclic ketone is obtained from the thorium salt of japanic acid (from Japan wax), the constitution of which is now proved to be nonadecane-1 : 19-dicarboxylic acid. A reaction similar to that given by the nonane homologue leads to the formation from yttrium decane-1 : 10-dicarboxylate of a small quantity of *cyclo*docosane-1 : 12-dione, containing a ring of 22 carbon atoms. Only slight traces of cyclic ketones are reported from the action of heat on the thorium or yttrium salts of tetradecane-1 : 13- or -2 : 13-dicarboxylic acid, 2-methyldodecane-1 : 12-dicarboxylic acid, and other pentadecane-, hexadecane-, and tetradecane-dicarboxylic acids, which sometimes give aliphatic ketones in small amount. For instance, from 2 : 13-dimethyltetradecane-1 : 14-dicarboxylic acid, small quantities of methyl 2 : 13-dimethyltetradecyl ketone were obtained, and similar aliphatic ketones have been observed as accompanying the cyclic ketones in cases where these are formed.[50]

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[47] J. Campardou and M. Séon, *Compt. rend.*, 1928, **186**, 591; **A.**, 393.

[48] I. Vogel, *J.*, 1928, 2032; **A.**, 1135.

[49] *Ann. Reports*, 1926, **23**, 112.

Several communications by R. Adams and his collaborators deal with acids synthesised in the course of their search for substances toxic towards *B. lepræ*. The number of new individual substances obtained is so large that little more can be done than to indicate the nature of the various series investigated. These include *cyclo*hexylalkylacetic acids, *cyclo*hexylmethyl-alkylacetic acids, *cyclo*pentylalkylacetic acids, β-*cyclo*pentylethyl-ethylalkylacetic acids, corresponding β-Δ^2-*cyclo*pentenyl acids, *cyclo*propylmethyl-alkylacetic acids, and di(*cyclo*hexylalkyl)-acetic acids. In general it may be said that in all series maximum toxicity towards *B. lepræ* is shown by acids containing 16—18 carbon atoms. Bactericidal power appears to depend little on the position of the carboxyl group in the hydrocarbon chain, and again *cyclo*alkylalkylacetic acids of equal molecular weight or with equally long side chains differ only slightly in toxicity whether the *cyclo*alkyl group is *cyclo*hexyl, *cyclo*pentyl, *cyclo*pentenyl, or *cyclo*propyl. In the last series mentioned above, no increased toxicity was developed by the introduction of a second *cyclo*hexyl group, giving compounds of the type $C_6H_{11}\cdot[CH_2]_x\cdot CH(CO_2H)\cdot[CH_2]_y\cdot C_6H_{11}$, despite the fact that the presence of one such group at the end of certain straight-chain aliphatic acids induces toxicity towards the bacillus.[51] The interest at present evoked by acids of this type is further shown by a long paper on the reactions involved in the degradation of chaulmoogric acid, 12-Δ^2-*cyclo*pentenyldodecane-1-carboxylic acid, a synthesis of which was mentioned in last year's Report (p. 88), to homohydnocarpylamine, $C_5H_7\cdot[CH_2]_{11}\cdot NH_2$, a modified form of Curtius reaction being employed.[52]

That the substance $C_8H_{12}O_4$ obtained by oxidation of α-Δ^3-carene cannot be either α- or β-*iso*propylglutaconic acid has been shown in the following way :[53] The synthesis of α-*iso*propylglutaconic acid has been achieved by removing hydrogen chloride from ethyl β-chloro-α-*iso*propylglutarate (A), the preparation of the latter substance being effected by the following series of reactions :

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[50] L. Ruzicka, M. Stoll, H. Schinz, *Helv. Chim. Acta*, 1928, **11**, 670; **A.**, 887; L. Ruzicka, H. Schinz, and M. Pfeiffer, *ibid.*, p. 686; **A.**, 887.

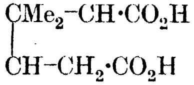
[51] R. Adams, W. M. Stanley, and H. A. Stearns, *J. Amer. Chem. Soc.*, 1928, **50**, 1475; **A.**, 754; G. R. Yohe and R. Adams, *ibid.*, p. 1503; **A.**, 754; J. A. Arvin and R. Adams, *ibid.*, pp. 1790, 1983; **A.**, 1003, 1003; L. A. Davies and R. Adams, *ibid.*, p. 2297; **A.**, 1132.

[52] C. Naegeli and G. Stefanovitsch, *Helv. Chim. Acta*, 1928, **11**, 609; **A.**, 881.

[53] K. V. Hariharan, K. N. Menon, and J. L. Simonsen, *J.*, 1928, 431; **A.**, 395.

$$\mathrm{CO_2Et{\cdot}CHPr^{\beta}{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et \longrightarrow CO_2Et{\cdot}CHPr^{\beta}{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2Et}$$
$$\longrightarrow \mathrm{CO_2Et{\cdot}CHPr^{\beta}{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2Et} \quad \text{(A)}$$

The resulting α-*iso*propylglutaconic acid was separated into *cis*- and *trans*-forms by means of acetyl chloride. The corresponding β-*iso*propyl acid has also been prepared, but neither of these acids was identical with the above substance $C_8H_{12}O_4$, for which the cyclic structure

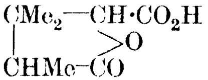


$\begin{array}{l}\mathrm{CMe_2{-}CH{\cdot}CO_2H}\\ |\\ \mathrm{CH{-}CH_2{\cdot}CO_2H}\end{array}$

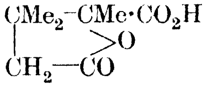
has been tentatively advanced.[54]

The difficult problem of the constitution of Balbiano's acid has been resolved by a synthesis which serves to establish its structure.[55] This dibasic acid, $C_8H_{12}O_5$, was obtained by Balbiano [56] in the course of oxidation experiments carried out with camphoric acid. When reduced it gives a monobasic lactonic acid, $C_8H_{14}O_4$, which, on further reduction, yields αββ-trimethylglutaric acid. Of the possible alternative formulæ (I) and (II) for the lactonic acid, the second is ruled out by synthesis,[57] and (I) is therefore Balbiano's lactonic acid.

(I.)



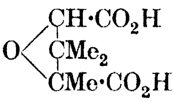
$\begin{array}{l}\mathrm{CMe_2{-\!\!-}CH{\cdot}CO_2H}\\ |\qquad\quad >\mathrm{O}\\ \mathrm{CHMe{-}CO}\end{array}$



$\begin{array}{l}\mathrm{CMe_2{-}CMe{\cdot}CO_2H}\\ |\qquad\quad >\mathrm{O}\\ \mathrm{CH_2{-\!\!-}CO}\end{array}$

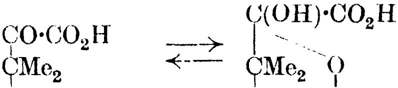
(II.)

The structure of the parent acid could not, however, be settled by this observation, and for many years the rival formulæ of Balbiano (III) and of Mahla and Tiemann (IV) [58] held the field. In more recent years the latter was modified by Kon, Stevenson, and Thorpe,[59] who preferred to represent the acid in the liquid state or in solution, as an equilibrium mixture of the tautomeric forms (IV) and (V). It was apparent by this time that Balbiano's oxide structure of the acid could not satisfy the experimental requirements, and synthetic proof of the keto-structure has now been supplied.



$\mathrm{O}\!\begin{array}{l}\diagup\,\mathrm{CH{\cdot}CO_2H}\\ \quad\ \mathrm{CMe_2}\\ \diagdown\,\mathrm{CMe{\cdot}CO_2H}\end{array}$

(III.)



$\begin{array}{l}\mathrm{CO{\cdot}CO_2H}\\ \mathrm{CMe_2}\\ \mathrm{CHMe{\cdot}CO_2H}\end{array} \rightleftarrows \begin{array}{l}\mathrm{C(OH){\cdot}CO_2H}\\ |\qquad \diagdown\\ \mathrm{CMe_2}\quad \mathrm{O}\\ \mathrm{CHMe{\cdot}CO}\end{array}$

(IV.) (V.)

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[54] J. L. Simonsen and M. G. Rau, *J.*, 1923, **123**, 553.

[55] J. C. Bardhan, *J.*, 1928, 2591, 2604; **A.**, 1243, 1215.

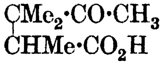
[56] *Rend. R. Accad. Lincei*, 1892, i, 278; *A.*, 1893, i, 174.

[57] G. Blanc, *Bull. Soc. chim.*, 1901, **25**, 68; *A.*, 1901, i, 119.

[58] *Ber.*, 1895, **28**, 2151; *A.*, 1895, i, 678.

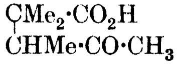
[59] *J.*, 1922, **121**, 656.

The synthesis of αββ-trisubstituted ketoglutaric acids such as (IV) is a matter of considerable difficulty, success being achieved in the present case by oxidising the acetyl group of αββ-trimethyl-lævulic acid (VI) to the $CO\cdot CO_2H$ group. This necessitated a synthesis of αββ-trimethyl-lævulic acid, which was prepared, along with its isomeride (VII), from the acid chloride (VIII) by the action of zinc methyl iodide.



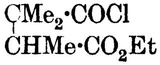
$$\begin{array}{l} CMe_2\cdot CO\cdot CH_3 \\ CHMe\cdot CO_2H \end{array}$$

(VI.)



$$\begin{array}{l} CMe_2\cdot CO_2H \\ CHMe\cdot CO\cdot CH_3 \end{array}$$

(VII.)

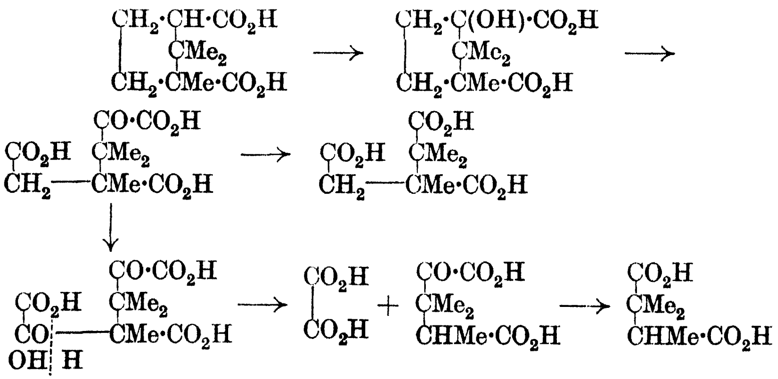


$$\begin{array}{l} CMe_2\cdot COCl \\ CHMe\cdot CO_2Et \end{array}$$

(VIII.)

The acid chloride was obtained from the half ester $CO_2H\cdot CMe_2\cdot CHMe\cdot CO_2Et$ prepared by the action of sodium ethoxide on trimethylsuccinic anhydride. Since the last reaction may result in the formation to some extent of $CO_2Et\cdot CMe_2\cdot CHMe\cdot CO_2H$, the presence of isomerides is readily explicable. Separation of the αββ- and the ααβ-trimethyl-lævulic acids was accomplished by fractional crystallisation of the semicarbazones and complete proof of their identity was furnished by an independent synthesis of the ααβ-compound.

Balbiano's acid was readily obtained by oxidation of αββ-trimethyl-lævulic acid, and since the synthesis just described is consistent only with the keto-formula the solid acid most probably exists in this form. The proof now given of the structure of the acid serves in no way to diminish the remarkable nature of the changes by which it is formed from camphoric acid, and the author now advances the following scheme as providing the simplest explanation of the transformation.[60]



The number of papers which have appeared during the year bears ample testimony to the continued interest taken in the natural fats and the acids derived from them. Studies of the decomposition of oleic acid in the presence of 30% of aluminium chloride show that the reaction, which begins at the ordinary temperature, becomes very vigorous at 150° and results in the formation of carbon dioxide, inflammable unsaturated gases, and liquid products. Hydrocarbons of the paraffin and *cyclo*paraffin types are formed, but neither hydroaromatic derivatives nor solid paraffins could be obtained. The reaction proceeds even more readily with palmitic and stearic acids, yielding unsaturated gases, a small liquid distillate, and considerable quantities of a solid paraffinic hydrocarbon. It is suggested that the latter two acids may be the parent substances of petroleums rich in solid paraffins.[61]

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[60] J. C. Bardhan, *loc. cit.* compare J. Bredt, *Ber.*, 1893, **26**, 3050; *A.*, 1894, i, 141.

As a result of a quantitative study [62] of the oxidation of methyl oleate and methyl elaidate by means of hydrogen peroxide in the presence of acetic acid, it is again suggested that under these conditions oleates yield the dihydroxystearic acid of m. p. 95° and elaidates give the isomeride, m. p. 132°, neither reaction involving any change in the molecular configuration. This conclusion is in conflict with the general views of Lapworth and Mottram [63] and of Böeseken and Belinfante,[64] who consider that the oxidation with permanganate, which produces the acid of m. p. 132° from oleic acid, does not involve configurational transformation. It is pointed out that the experimental conditions of the permanganate oxidation necessitate in this particular case the use of a large excess of alkali, which, in the opinion of Hilditch, may promote isomeric change. On the other hand, it must be urged that experimental evidence in support of the opposite view has been contributed.[65] It is shown that, in a series of alicyclic compounds containing an ethylenic linking, permanganate gives invariably *cis*-glycols whereas peracids give rise to *trans*-isomerides.

The pyrogenic decomposition of methyl ricinoleate has been investigated in order to determine the position of the double bond, and its behaviour under the influence of heat, the ester being used owing to the tendency of the free acid to polymerise. Heptaldehyde and methyl undecenoate were obtained in good yield by choice of suitable conditions of heating and no sign of either racemisation or migration of the double bond could be detected.[66]

An acid of common occurrence in marine animal oils is named cetoleic acid, $C_{22}H_{42}O_2$. It is isomeric with erucic acid and although the latter has been frequently recorded as occurring in marine animal oils, its presence is now considered doubtful. The suggestion is made that the supposed erucic acid was in reality cetoleic acid which, when oxidised by potassium permanganate in acetone, yields *n*-undecoic acid and nonane-1 : 9-dicarboxylic acid. After treatment with ozone the same two acids and also *n*-undecaldehyde were identified, the constitution of cetoleic acid being thus proved to be $CH_3{\cdot}[CH_2]_9{\cdot}CH{:}CH{\cdot}[CH_2]_9{\cdot}CO_2H$. The same author[67] has investigated the structure of zoomaric acid, a hexadecenoic acid found in cod-liver oil, and various whale oils. This proves to be $CH_3{\cdot}[CH_2]_5{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2H$, identical with an acid named palmitoleic and isolated from a specimen of South Georgia whale oil.[68] Amongst other acids, obtainable from natural sources, whose structures have now been elucidated may be mentioned jalapinolic acid, which has been shown to be *d*-10-hydroxyhexadecoic acid. In the course of the work various hydroxy- and keto-fatty acids were prepared and both 11-hydroxypentadecoic and 11-hydroxyhexadecoic acids were synthesised. The former of these differs structurally from convolvulinolic acid, which occurs along with jalapinolic acid in the jalapin glucosides.[69]

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[61] N. D. Zelinski and K. P. Lavrovski, *Ber.*, 1928, **61**, [*B*], 1054; **A.**, 731.

[62] T. P. Hilditch and C. H. Lea, *J.*, 1928, 1576; **A.**, 868.

[63] *Mem. Manchester Lit. Phil. Soc.*, 1927, **71**, 63; **A.**, 1928, 221.

[64] *Rec. trav. chim.*, 1926, **45**, 917; **A.**, 1927, 132.

[65] See J. Böeseken, *ibid.*, 1928, **47**, 683; **A.**, 734.

[66] P. S. Paniutin, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1; **A.**, 617.

The use of triphenylmethyl ethers, which have proved so advantageous in synthetic work in the carbohydrate group, has now been extended to the synthesis of partly acylated glycerides. The preparation of glycerol αβ-dibenzoate may be cited as an example of the method. Glycerol α-monotriphenylmethyl ether is first prepared and the dibenzoate of this substance when treated with hydrobromic acid in acetic acid at 0° readily yields glycerol αβ-dibenzoate. By suitable modifications of the process glycerol β-benzoate, glycerol β-*p*-nitrobenzoate, and other similar compounds may be prepared.[70]

It is only within recent years that methods have become available for determining quantitatively the composition of natural fats, and figures are available for only a few of the fats in common use. Information concerning the way in which the fatty acids are combined with glycerol in the fats is still more lacking owing to the very considerable experimental difficulties which have to be faced. In a recent paper[71] results are given which have been obtained by the application of new principles in an attempt to elucidate this complex problem. The underlying idea has been to alter the chemical characteristics of the glycerides in such a manner that new glycerides, more readily separable, may be obtained without disturbance of the combined glyceryl radical. Two such processes are described: (*a*) controlled oxidation by potassium permanganate in acetone, which does not affect saturated glycerides, but converts the mono-, di-, and tri-oleins into the corresponding acid azelaic esters; (*b*) controlled oxidation with an acetic acid solution of hydrogen peroxide, which is again without effect on the saturated glycerides but gives dihydroxystearic esters with oleins. In so far as the results obtained can be summarised in the space now available, it appears, contrary to a widespread impression, that in vegetable glycerides the fatty acids are distributed impartially rather than selectively and that in consequence the occurrence of simple triglycerides and mixed saturated glycerides is reduced to a minimum. Thus the physical properties of such a fat must depend primarily upon the particular mixture of fatty acids from which it takes its origin. For instance, Cacao butter, which contains palmitic, stearic, and oleic acids in approximately equal proportions, consists mainly of mono-oleic disaturated glycerides and this fat more closely resembles an individual glyceride than one in which the proportions of the component acids are very different. Again, in cotton-seed oil entirely saturated glycerides are present only in very small proportion, and the palmitic acid is uniformly combined with the unsaturated acids, the proportion of palmitic and unsaturated acids being approximately 1 to 3. In mutton tallow, taken as a representative of the animal fats, a very different state of affairs prevails and a much greater proportion of fully saturated glycerides is present.

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[67] Y. Toyama, *J. Soc. Chem. Ind. Japan*, 1927, **30**, 597, 603; **A.**, 1928, 154.

[68] E. F. Armstrong and T. P. Hilditch, *J. Soc. Chem. Ind.*, 1925, **44**, 180T; *A.*, 1925, i, 778.

[69] L. A. Davies and R. Adams, *J. Amer. Chem. Soc.*, 1928, **50**, 1749; **A.**, 990.

[70] B. Helferich, P. E. Speidel, and W. Toeldte, *Ber.*, 1923, **56**, 766; *A.*, 1923, i, 331; B. Helferich and H. Sieber, *Z. physiol. Chem.*, 1927, **170**, 31; 1928, **175**, 311; **A.**, 44, 734.

[71] T. P. Hilditch and C. H. Lea, *J.*, 1927, 3106; **A.**, 1928, 152.

Another method which is being employed with success in the study of natural glycerides consists in the bromination of the fat in light petroleum, followed by separation of the bromides by dissolution in various solvents. The constitution of the individual brominated glycerides may then be determined by means of hydrolysis with hydrochloric acid. Linseed oil has in this way yielded dilinoleolinolenin bromide, two linoleodilinolein bromides and dilinoleo-olein bromide. Soya-bean oil, train oil, oil of silkworm pupa, and cod-liver oil have also been investigated and the large number of individual glycerides separated and identified by Suzuki and his collaborators provides a tribute both to the skill of the workers and to the power of the experimental method.[72]

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[72] B. Suzuki and Y. Yokoyama, *Proc. Imp. Acad. Tokyo*, 1927, **3**, **526**, **529**; 1928, **4**, 161; **A.**, 152, 736; B. Suzuki and Y. Masuda, *ibid.*, 1927, **3**, **531**; 1928, **4**, 161, 165; **A.**, 153, 736. See also (for soya-bean oil) K. Hashi, *J. Soc. Chem. Ind. Japan*, 1927, **30**, 849, 856; **A.**, 1928, 736.

Nitrogen Compounds.

Important developments have taken place during the year in the chemistry of the aliphatic diazo-compounds. It has been known for some time that certain aldehydes react with diazomethane to form methyl ketones,[73]

$$R{\cdot}CHO + CH_2N_2 \longrightarrow R{\cdot}CO{\cdot}CH_3 + N_2,$$

and an analogous reaction was later applied to certain acid chlorides and expressed as follows : [74]

$$R{\cdot}COCl + CH_2N_2 \longrightarrow R{\cdot}CO{\cdot}CH_2Cl + N_2.$$

This observation has now been followed by detailed investigations which have revealed [75] that the course of the reaction with acyl chlorides is in point of fact very different from that indicated in the above equation, and that the primary product is a diazo-ketone. The chloro-ketone, if formed at all, is the result of subsequent decomposition of the diazo-ketone in the presence of halogen acid. The general nature of the reaction for the acylation of diazomethane has thus been established and may be summarised by equations (A), (B), and (C), of which under all conditions (A) and (B) predominate over the secondary reaction (C) :

$$R{\cdot}COCl + CH_2N_2 \longrightarrow R{\cdot}CO{\cdot}CHN_2 + HCl \quad . \quad . \quad (A)$$
$$CH_2N_2 + HCl \longrightarrow CH_3Cl + N_2 \quad . \quad . \quad . \quad . \quad (B)$$
$$R{\cdot}CO{\cdot}CHN_2 + HCl \longrightarrow R{\cdot}CO{\cdot}CH_2Cl + N_2 \quad . \quad . \quad (C)$$

The best conditions for the preparation of the diazo-ketones involve the addition of the acid chloride (1 mol.) to an ethereal solution of diazomethane (2 mols.), and Nierenstein [76] has recently claimed that by adding the reagents in the reverse order the course of the reaction may be altered with the production of the chloro-ketone in high yields. Other workers,[77] however, have failed to confirm this view and maintain that under all conditions (A) is the primary reaction. If a chloro-ketone is required, the best procedure is to make the diazo-ketone and submit it to the action of hydrogen chloride.

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[73] H. Meyer, *Monatsh.*, 1905, **26**, 1300; *A.*, 1906, i, 87.

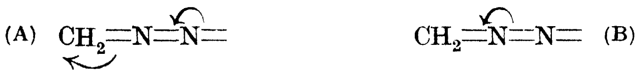
[74] D. A. Clibbens and M. Nierenstein, *J.*, 1915, **107**, 1491; *A.*, 1915, i, 1062. See also R. T. Dale and M. Nierenstein, *Ber.*, 1927, **60**, [*B*], 1026; **A.**, 1927, 564.

[75] W. Bradley and R. Robinson, *J.*, 1928, 1310, 1545; **A.**, 759; F. Arndt and J. Amende, *Ber.*, 1928, **61**, [*B*], 1122; **A.**, 759. Compare F. Arndt, B. Eistert, and J. Partale, *Ber.*, 1927, **60**, [*B*], 1364; **A.**, 1927, 774.

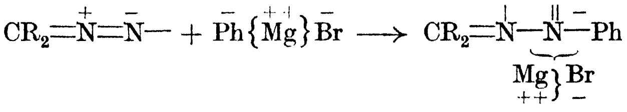
[76] *Nature*, 1928, **121**, 940; **A.**, 739.

[77] W. Bradley and G. Schwarzenbach, *J.*, 1928, 2904; **A.**, 1929, 68.

Since the diazenes $R_2{\cdot}CN_2$ react vigorously both with electron seeking agents such as halogen molecules and with electron-donating agents (for instance, organo-metallic compounds), these compounds present interesting problems from the point of view of the electron theory of valency,[78] on which basis the Angeli–Thiele formula may be written $CR_2{=}\overset{+}{N}{=}\overset{-}{N}{=}$, where a line represents two electrons. Different positions in the diazomethane molecule are involved in the two types of reactions referred to and it is found that the anionoid centre is situated on the carbon atom next to the positively charged nitrogen atom, and the negatively charged nitrogen is the kationoid centre. The apparent anomaly is explained by assuming that the maintenance of atomic electron configurations is more important than neutralisation of the charges and it is shown that in each case the ultimate result of the electronic displacements postulated in the anionoid (A) and in the kationoid type of reactivity (B) is a more even distribution of the charge :


(A) (B)

The reaction with magnesium phenyl bromide may be considered as an example of kationoid reactivity,



$$CR_2{=}\overset{+}{N}{=}\overset{-}{N}{-} + \overset{-}{Ph}\{\overset{++}{Mg}\}\overset{-}{Br} \longrightarrow CR_2{=}\underbrace{\overset{|}{N}{-}\overset{||}{N}}_{\underset{++}{Mg}\}\underset{-}{Br}}{-}\overset{-}{Ph}$$

but the action of acids on diazomethane is probably represented by the scheme (A).

$$X{-}\textcircled{\scriptsize H} + CH_2{=}\overset{+}{N}{=}\overset{-}{N}{=} \longrightarrow \overset{-}{X}\{H{-}CH_2{-}\overset{+}{N}{\equiv}N{-} \longrightarrow$$
$$\overset{-}{X}\,\overset{+}{C}H_3 + {-}N{\equiv}N{-} \longrightarrow XCH_3 + N_2$$

In this case the process depends upon the intermediate formation of a diazonium salt, which then decomposes in the usual way. Rather more complex cases are to be found in the reactions between the diazenes and aldehydes and acyl chlorides.

A possible mechanism for the former is given in the annexed equations, although it is necessary to remember that the first stage may proceed only to a minute extent, instead of involving the complete transfer of charge here represented. Once the carbon atoms are joined, the main changes leading to the separation of nitrogen and the wandering of a proton may proceed by the more direct route indicated in the expression (B)

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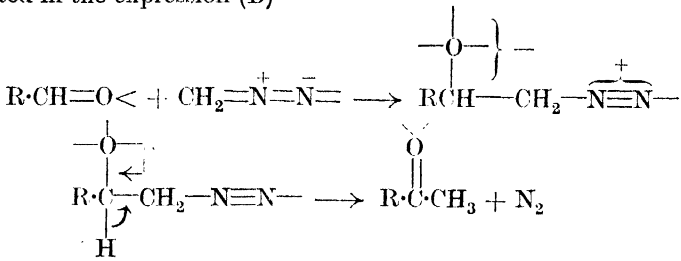
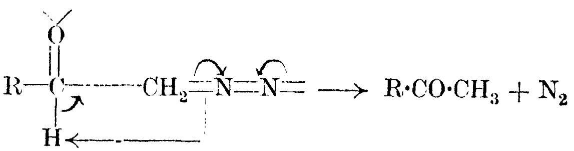
[78] **W. Bradley and R. Robinson,** ***loc. cit.***

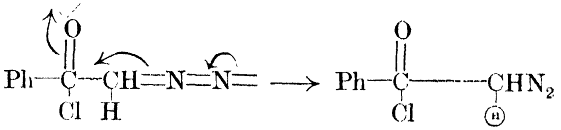
(A)


R·CH=O< + CH₂=N=N= ⟶ R·CH—CH₂—N≡N—
R·C—CH₂—N≡N— ⟶ R·C·CH₃ + N₂
H

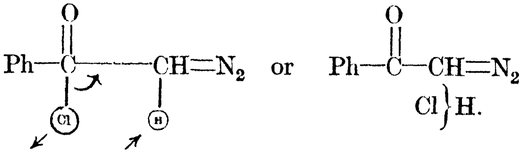
(B)



As an example of the latter type of reaction the formation of diazoacetophenone from benzoyl chloride and diazomethane may be represented by the following two stages, the explanation given being quoted from the paper by Bradley and Robinson.



" At this stage the terminal nitrogen has succeeded in transferring a fraction of its negative charge to the oxygen atom and a bond between the carbon atoms has been initiated. The repulsion exerted by the central nitrogen on the proton indicated is now reinforced by the oxygen and chlorine nuclei and the following changes may be almost synchronous."



This conception of a reaction mechanism, in which the direction is initiated and controlled by a process involving fractional valencies but the course is completed by a different and more direct route, was put forward in explanation of *m*-substitution in the benzene series some years ago,[79] and is now shown to be of wide general application.

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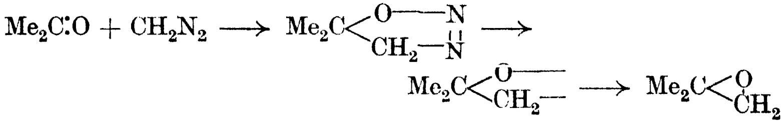
[79] R. Robinson, *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 4; *A.*, 1921, ii, 545.

As the result of studies on the action of diazomethane on aldehydes it is concluded [80] that the course of the reaction is governed principally by the nature of the aldehyde and to a lesser extent by experimental conditions. Amongst the examples quoted in support of this view the following may be mentioned as illustrative. Although *m*-nitrobenzaldehyde affords exclusively *m*-nitroacetophenone, the *p*-isomeride gives a mixture of *p*-nitroacetophenone and *p*-nitrophenylethylene oxide. Chloral is converted into ααα-trichloropropylene βγ-oxide, and the earlier claim [81] that trichloroacetone is obtainable in this reaction is not substantiated. The available evidence appears to indicate that substituted ethylene oxides are formed most readily from those aldehydes which show a pronounced tendency towards the formation of hydrates.

The behaviour of diazomethane has been examined from yet another point of view by H. Meerwein and W. Burneleit.[82] These authors have investigated the possibility of activating atomic groups, in this case the carbonyl group, by means of complex formation. At low temperatures a solution of diazomethane in acetone undergoes little or no change, but on addition of some 10% of water nitrogen is freely evolved, and the reaction thus initiated continues as diazomethane is added, until about 80% of the equivalent amount has been used. The products include *as*-dimethylethylene oxide, methyl ethyl ketone, and in all probability diethyl ketone and methyl *n*-propyl ketone. The authors represent the course of the change by the accompanying equations, the activity of the diazomethane being anionoid in character and proceeding in accordance with the scheme outlined above.



$$\mathrm{Me_2C{:}O + CH_2N_2 \longrightarrow Me_2C<\begin{matrix} O—N \\ CH_2—N \end{matrix} \longrightarrow Me_2C<\begin{matrix} O— \\ CH_2— \end{matrix} \longrightarrow Me_2C<\begin{matrix} O \\ CH_2 \end{matrix}}$$

Further reaction with diazomethane yields methyl ethyl ketone and then higher ketones. During the reaction the added water remains unmethylated and in a similar way alcohols, which may replace the water as catalysts, remain unaffected. Since dilute sodium hydroxide solution also promotes the reaction, the activating effect cannot be attributed to hydrogen ions.

The interaction of nitroguanidine with hydrazine in dilute aqueous solution at 50—60° yields the interesting nitroaminoguanidine, $NO_2{\cdot}NH{\cdot}C({:}NH){\cdot}NH{\cdot}NH_2$, probably *via* an intermediate additive compound. This new substance decomposes explosively at its melting point, reduces copper and silver solutions with formation of explosive metallic derivatives, and may be used in the quantitative estimation of nickel. In addition, the blue colour of the nickel salt in alkaline solution provides a delicate qualitative test for that metal.[83]

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[80] F. Arndt and B. Eistert, *Ber.*, 1928, **61**, [*B*], 1118; **A.**, 739; F. Arndt, B. Eistert, and J. Amende, *ibid.*, p. 1949; **A.**, 1240.

[81] F. Schlotterbeck, *Ber.*, 1909, **42**, 2559; *A.*, 1909, i, 553.

[82] *Ber.*, 1928, **61**, [*B*], 1840; **A.**, 1217.

In the course of work on the synthesis of creatinol [84] [*N*-methyl-*N*-(β-hydroxyethyl)guanidine] it was found that the most satisfactory method for the preparation of amino-alcohols of the aminoethanol type is to treat ethylene chlorohydrin with liquid carbonyl chloride and to allow the resulting β-chloroethyl chloroformate to react with amines in benzene solution. The product is now a β-chloroethyl alkylcarbamate, $CH_2Cl{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}NHR$, which can be decomposed by excess of alkali hydroxide to give the corresponding amino-alcohol, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}NHR$. These aminoethanols may then be transformed into the guanido-alcohol either by the Erlenmeyer method, in which a salt of the amine is allowed to react with cyanamide, or by Rathke's method, in which the amino-alcohol is treated with a salt of *S*-alkyl *iso*thiocarbamide. The mechanism of the latter reaction is still by no means clear and in the author's paper the earlier addition theories [85] are rejected and a decomposition theory is advocated in which the formation of cyanamide from the alkyl *iso*thiocarbamide is postulated as a first stage, which is then followed by the usual Erlenmeyer reaction. The synthesis of creatinol hydrobromide, which is cited as an example of this type of reaction, is achieved by allowing *S*-ethyl *iso*thiocarbamide hydrobromide to react with methyl-β-hydroxyethylamine in the presence of a little water. The free base is sensitive to the action of alkali, but the salts are stable towards acids.

Pure crystalline alanine may be obtained from pyruvic acid by submitting the latter to the simultaneous action of hydrogen and ammonia in the presence of colloidal palladium stabilised by starch paste.[86]

A more convenient method for the preparation of arginine from gelatin has been described [87] and in the same paper the transformation of arginine into glycocyamidine hydrochloride is reported. This is carried out by careful treatment of triacetyl anhydro-arginine with glycine ester, the resulting ethyl ester of diacetyl glycocyamine being heated with hydrochloric acid at 100°. The hydrochloride of glycocyamidine (I) thus obtained has also been prepared by heating glycocyamine (II) in a sealed tube with fuming hydrochloric acid at 140°.

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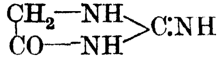
[83] R. Phillips and J. F. Williams, *J. Amer. Chem. Soc.*, 1928, **50**, 2465; **A.**, 1229.

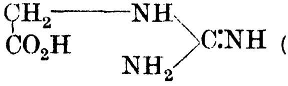
[84] H. Schotte, H. Priewe, and H. Roescheisen, *Z. physiol. Chem.*, 1928, **174**, 119; **A.**, 1122.

[85] H. Lecher and F. Graf, *Ber.*, 1923, **56**, 1326; *A.*, 1923, i, 761; H. Lecher, *Z. physiol. Chem.*, 1928, **176**, 43; **A.**, 1123.

[86] Aubel and Bourguel, *Compt. rend.*, 1928, **186**, 1844; **A.**, 868.

[87] M. Bergmann and L. Zervas, *Z. physiol. Chem.*, 1927, **172**, 277; **A.**, 1928, 512.

(I.)

$\begin{array}{l} CH_2-NH \\ CO-NH \end{array} > C{:}NH$

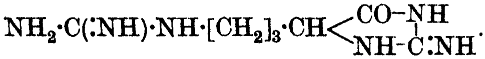

$\begin{array}{ll} CH_2 & -NH \\ CO_2H & \\ & NH_2 \end{array} > C{:}NH$
(II.)

Another method[88] for the preparation of glycocyamidine consists in the interaction of guanidine and ethyl aminoacetate at 0°, a reaction which suggested a possible method for the detection of esters from polypeptides. That this expectation was not realised may perhaps be due to the delicate nature of the reaction, which is inhibited completely by the presence of ammonia. The reaction mechanism suggested by the authors involves the loss of ammonia from the guanidine, followed by the union of the amino-acid with nascent cyanamide.

When α-amino-acids are warmed with acetic anhydride and pyridine, carbon dioxide is eliminated and an α-acetamido-ketone is produced by the attachment of acetyl groups to the nitrogen and to the α-carbon atom :

$$R\cdot CH(NH_2)\cdot CO_2H + (CH_3\cdot CO)_2O \longrightarrow R\cdot CH(NH\cdot CO\cdot CH_3)\cdot CO\cdot CH_3$$

Certain other acids undergo a similar change, benzyl methyl ketone being formed in this way from phenylacetic acid, but alkylamino-acids, β-amino-acids, and amino-acids which contain no replaceable hydrogen in the α-position undergo simple acetylation without further change. Furthermore, the azlactones formed from leucine, phenylalanine and aspartic acid by the action of acetic anhydride, yield with acetic anhydride and pyridine the same acetamido-ketones as do the corresponding amino-acids. The suggestion is therefore made that the azlactones are formed as intermediate compounds during the reaction, which may involve also the formation of a β-ketonic acid at one stage.[89]

Experiments carried out by L. Zervas and M. Bergmann[90] have served to show that the substance produced by the auto-condensation of arginine ester and considered by Fischer and Suzuki to be arginylarginine is in reality optically inactive αδ-diguanido-*n*-valeric anhydride,  $NH_2\cdot C({:}NH)\cdot NH\cdot[CH_2]_3\cdot CH\!<\!\begin{array}{l} CO-NH \\ NH-C{:}NH \end{array}$. The latter substance has been synthesised by the condensation of arginine with *S*-ethyl *iso*thiocarbamide and found to be identical with the so-called "arginylarginine." It appears that, on the liberation of arginine ester from its hydrochloride, interaction takes place between the ester group of one molecule and the guanido-group of another, giving a very unstable ester of arginylarginine, from which $\alpha\delta$-diguanidovaleric anhydride is produced by loss of ornithine methyl ester, followed by internal ring closure in the residue.

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[88] E. Abderhalden and H. Sickel, *Z. physiol. Chem.*, 1928, **173**, 51; **A.**, 511.

[89] H. D. Dakin and R. West, *J. Biol. Chem.*, 1928, **78**, 91, 745; **A.**, 874, 1120.

[90] *Ber.*, 1928, **61**, [*B*], 1195; **A.**, 874.

Hydantoin-3-acetic acid yields on hydrolysis a glycylglycine-*N*-carboxylic acid which has been formulated variously as

$$CO_2H\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H\ ^{91}$$

and as $CO_2H\cdot NH\cdot CH_2\cdot C(OH):N\cdot CH_2\cdot CO_2H$.[92] It is now found that hydantoin-3-acetic acid is transformed by ammonia into a diamide identical with that formed from ammonia and carbonyl bisglycine ester, and that the ester prepared by the action of carbonyl chloride on glycine ester is identical with the ester of glycylglycine-*N*-carboxylic acid. For these reasons it is now suggested that the correct structure of the last-named acid is given by the formula $CO(NH\cdot CH_2\cdot CO_2H)_2$.[93]

Further investigation of oxidation and reduction reactions with cystine and cysteine indicates that, in the absence of some third component, neither reduced indigo nor reduced indigo-carmine can be oxidised by cystine. The activating agent is not iron, which can, however, influence the reaction velocity, but seems to be an unstable oxygen or sulphur additive product of indigo-carmine whose essential function is to activate the sulphur atom, whereupon the latent reducing or oxidising power of the $-SH$ or $=S_2$ groups is brought into play.[94]

An improved method has been employed in the isolation of phosphocreatine, which has been obtained as the calcium derivative, to which is assigned the composition $C_4H_8O_5N_3PCa,4H_2O$. The structure suggested is $PO(OH)_2\cdot NH\cdot C(:NH)\cdot NMe\cdot CH_2\cdot CO_2H$, which renders this substance the first compound containing phosphorus attached to nitrogen to be isolated from natural sources.[1] The question of its importance in the series of chemical changes involved in muscular contraction is as yet undecided.[2]

Organo-metallic Compounds.

Beryllium alkyl derivatives are obtained by allowing anhydrous beryllium chloride to react with magnesium alkyl halides in the

[91] E. Fischer and E. Fourneau, *Ber.*, 1901, **34**, 2868; *A.*, 1901, i, 675.

[92] H. Leuchs and P. Sander, *Ber.*, 1925, **58**, 1528; *A.*, 1925, i, 1248.

[93] F. Wessely and E. Komm, *Z. physiol. Chem.*, 1928, **174**, 306; **A.**, 623.

[94] E. C. Kendall and D. F. Loewen, *Biochem. J.*, 1928, **22**, 649; **A.**, 1122.

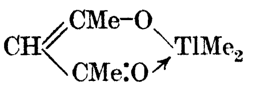
[1] C. H. Fiske and Y. Subbarow, *Science*, 1928, **67**, 169; **A.**, 744.

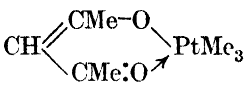
[2] D. Ferdmann (with O. Feinschmidt), *Z. physiol. Chem.*, 1928, **178**, 52; **A.**, 1267.

complete absence of oxygen. The interaction of the metal with mercury alkyls fails to give the beryllium compounds, although this method may be used to prepare the aryl derivatives. The alkyl derivatives combine very readily with oxygen. The dimethyl and diethyl compounds are spontaneously inflammable, but beryllium di-*n*-butyl oxidises more smoothly, yielding butyl alcohol and probably beryllium *n*-butyl oxide. The beryllium alkyls react violently with water to form the corresponding hydrocarbon. Carbon dioxide reacts with beryllium dimethyl and yields acetic acid, but with the diethyl derivative triethylcarbinol is formed. Differences in reactivity between the dimethyl and the diethyl compound are revealed also in certain other reactions, such as their interaction with benzophenone, the former giving in this case diphenylmethylcarbinol and the latter, by reduction of the ketone, benzhydrol.[3] Beryllium alkyl halides, BeRX, are also described. They are prepared by heating beryllium with alkyl iodides in the presence of mercuric chloride, and in general they are less reactive than either the beryllium dialkyls or the Grignard compounds.[4]

Some organo-metallic compounds of thallium and of platinum have been prepared, and have special interest from the point of view of the co-ordination theory of valency. They are obtainable either by the double decomposition of thallium dialkyl halides with compounds such as thallium acetylacetone, or by the action of thallium dialkyl ethoxide or dialkyl carbonate on the appropriate diketone. In this way thallium dimethyl acetylacetone and the corresponding diethyl derivative were obtained as well as thallium dimethyl benzoylacetone and analogous compounds. They are all crystalline compounds with unusual properties. When heated under diminished pressure they sublime, and in benzene and hexane they dissolve readily, giving non-ionised solutions. Their properties, therefore, are exactly those to be expected of chelate co-ordinated compounds with the structure (I) :

(I.)





(II.)

In aqueous solution the covalent state gives place to an ionised condition, the solutions are now alkaline in reaction, and the thallium dialkyl can be titrated quantitatively.[5]

The analogous platinum compound (II) is obtained from thallous acetylacetone and trimethyl platinic iodide. Like the corresponding thallium compounds, it may be sublimed unchanged.[6]

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[3] H. Gilman and F. Schulze, *J.*, 1927, 2663; **A.**, 1928, 50.

[4] *Idem*, *J. Amer. Chem. Soc.*, 1927, **49**, 2904; **A.**, 1928, 50.

[5] R. C. Menzies, N. V. Sidgwick, E. F. Cutcliffe, and J. M. C. Fox, *J.*, 1928, 1288; **A.**, 745. Compare F. Feigl and E. Bäcker, *Monatsh.*, 1928, **49**, 401; **A.** **1125.**

A further examination of the reaction between sodium and propionamide and butyramide in benzene shows that the main product is the derivative R·CO·NHNa and that there is no marked difference between the action of sodium and potassium. Evidence in favour of this view is furnished by the observation that propionyl chloride and the product formed by the action of sodium on propionamide yield dipropionamide.[7]

The interest taken in Grignard's reaction and its applications continues unabated and it will be possible to indicate only a few of the new observations which have recently been described. Uncertainty still remains concerning the structure and even the molecular weight of the magnesium alkyl halides. As the result of evidence gained by determinations of molecular weight in ethereal solution, Terentiev [8] advocated the formula $\mathrm{Mg(Alk_2MgI_2,2Et_2O)}$, but it now appears that such experiments are complicated by the strong tendency towards association shown by these compounds. Under suitable conditions the molecular weight corresponds to that required by the formula $\mathrm{Alk.MgI} = = = \mathrm{(OEt_2)_2}$. Thus in dilute solution magnesium ethyl bromide exists mainly as the complex $\mathrm{EtMgBr} = = = \mathrm{(OEt_2)_2}$, only small amounts being ionised or polymerised. Exactly analogous observations have been made with magnesium iodide dietherate and there appears to be no valid reason for postulating the existence of bimolecular compounds during the reaction between magnesium methyl iodide and water.[9]

The magnesium alkyl and aryl compounds in ethereal solution undergo autoxidation unless oxygen is rigidly excluded. A detailed study of this reaction has now been contributed in the course of which the authors make certain suggestions concerning the mechanism of the reaction between magnesium methyl iodide and oxygen. The first stage of this is considered to lead to the formation of the complex $\mathrm{(MeMgI \cdots\cdot 3O \cdots\cdot MeMgI,Et_2O)}$ which may decompose in at least two ways. In the one case, by means of a unimolecular reaction, the two iodine atoms are replaced by oxygen, and the liberated iodine reacts in the known manner with unchanged magnesium methyl iodide. The newly formed complex

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[6] R. C. Menzies, *J.*, 1928, 565; **A.**, 509.

[7] A. Parts, *Ber.*, 1927, **60**, [*B*], 2520; **A.**, 1928, 158.

[8] *Z. anorg. Chem.*, 1926, **156**, 73; **A.**, 1926, 1130.

[9] J. Meisenheimer, *Ber.*, 1928, **61**, [*B*], 708; **A.**, 624; J. Meisenheimer and W. Schlichenmaier, *ibid.*, p. 720; **A.**, 625. See also Q. Mingoia, *Gazzetta*, 1928, **58**, 532; **A.**, 1266. Contrast L. Kierzek, *Bull. Soc. chim.*, 1927, [iv], **41**, 1299; **A.**, 1927, 1176; and D. Ivanov, *Compt. rend.*, 1927, **185**, 505; **A.**, 1927, 961.

$(MeMg\cdots\cdot 3O\cdots\cdot MgMe,Et_2O)$ then decomposes, giving MgO and $Mg(OMe)_2$. In the second case, a bimolecular reaction is responsible for the oxidation, by the complex, of one molecule of MeMgI to MeO·MgI. The oxidation potential of the residue

$$(MeMgI\cdots\cdot 2O\cdots\cdot MeMgI,Et_2O)$$

is thereby so much diminished that expulsion of the iodine no longer occurs, and the oxidation now results in the formation of methoxy-residues. Both these reactions occur simultaneously in concentrated solutions of the magnesium alkyl iodides, but the bimolecular reaction is excluded in the case of iodides in dilute solution. The unimolecular reaction invariably predominates with bromides.[10]

The interaction of magnesium alkyl halides and alkyl sulphonates is usually represented by the equation

$$2RSO_3Alk + 2R'MgX \longrightarrow 2R'Alk + (RSO_3)_2Mg + MgX_2,$$

which, however, does not agree with the results of more recent investigations. It now seems [11] that the product R'Alk is obtained in yields never greater than 50% and that an equivalent amount of alkyl halide is formed simultaneously. The scheme

$$\text{(a)}\ RSO_3Alk + R'MgX \longrightarrow R'Alk + RSO_3MgX$$

and

$$\text{(b)}\ RSO_3Alk + RSO_3MgX \longrightarrow AlkX + (RSO_3)_2Mg$$

is now suggested and experimental evidence in its favour is provided by the separation of *n*-butyl iodide and magnesium naphthalene-2-sulphonate from the products of reaction of iodo-magnesium naphthalene-2-sulphonate and *n*-butyl *p*-toluenesulphonate. Improved yields of the derivative R'Alk are, however, claimed by S. S. Rossander and C. S. Marvel [12] for the particular case in which one molecule of a Grignard reagent containing six or more carbon atoms reacts with two molecules of γ-chloropropyl *p*-toluenesulphonate. This provides a method whereby a carbon chain may be lengthened by three carbon atoms. A different reaction mechanism, not favoured by Gilman and Heck, is advocated by these authors.

The utilisation of mixed magnesium alkyloxyhalides, RO·MgX, which are prepared by the action of magnesium alkyloxides on etherated magnesium halides, has been studied by V. Grignard and M. Fluchaire.[13] Neither the etherated halides nor the magnesium alkyloxides act as condensing agents and a mixture of the two is inactive until the reaction $MgX_2 + Mg(OR)_2 \longrightarrow 2RO{\cdot}MgX$ has taken place. With aldehydes in the presence of mixed magnesium alkyloxyhalides, two simultaneous reactions are observed : (I) aldol formation, and (II) ester formation, $2R{\cdot}CHO \longrightarrow R{\cdot}CO_2{\cdot}CH_2R$. For instance, acetaldehyde and magnesium butoxyiodide in the presence of ether yield ethyl acetate, aldol, and butyl acetate, the formation of the last substance being due to the interaction of ethyl acetate and the magnesium derivative. The production of esters is explained by the intermediate formation of a semi-acetal,[14] the subsequent condensation of which yields the ester :

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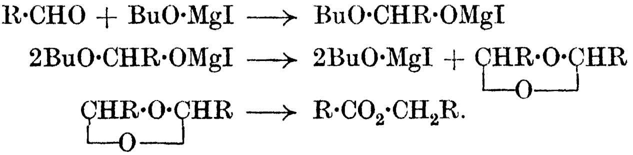
[10] J. Meisenheimer and W. Schlichenmaier, *Ber.*, 1928, **61**, [*B*], 2029; **A.**, 1232.

[11] H. Gilman and L. L. Heck, *J. Amer. Chem. Soc.*, 1928, **50**, 2223; **A.**, 1124.

[12] *Ibid.*, p. 1491; **A.**, 732.

[13] *Ann. Chim.*, 1928, [x], **9**, 5; **A.**, 396.



$$\begin{aligned}
\mathrm{R{\cdot}CHO + BuO{\cdot}MgI} &\longrightarrow \mathrm{BuO{\cdot}CHR{\cdot}OMgI}\\
\mathrm{2BuO{\cdot}CHR{\cdot}OMgI} &\longrightarrow \mathrm{2BuO{\cdot}MgI} + \underbrace{\mathrm{CHR{\cdot}O{\cdot}CHR}}_{\mathrm{O}}\\
\underbrace{\mathrm{CHR{\cdot}O{\cdot}CHR}}_{\mathrm{O}} &\longrightarrow \mathrm{R{\cdot}CO_2{\cdot}CH_2R.}
\end{aligned}$$

Aldol formation is represented by the equation

$$\mathrm{CHO{\cdot}CH_2R + BuO{\cdot}CH(OMgI){\cdot}CH_2R} \longrightarrow \mathrm{BuOH + CHO{\cdot}CHR{\cdot}CH(OMgI){\cdot}CH_2R}$$

Sometimes, as with furfuraldehyde, reduction to the alcohol takes place, $R{\cdot}CHO$ and $BuO{\cdot}MgBr$ giving $CH_2Pr{\cdot}O{\cdot}CHR{\cdot}OMgBr$, which then decomposes into $Pr{\cdot}CHO$ and $CH_2R{\cdot}OMgBr$.

Methyl alkyl ketones react in accordance with the scheme $2R{\cdot}COMe \longrightarrow R{\cdot}CO{\cdot}CH_2{\cdot}CMeR{\cdot}OH$ and from the alcohols so formed unsaturated ketones of the type $R{\cdot}CO{\cdot}CH{:}CMeR$ are readily obtainable. In certain cases, *e.g.*, when methyl *iso*butyl ketone reacts with magnesium butoxybromide and benzoyl chloride, the enolising effect of the organo-metallic compound becomes evident and an ester of the enolic form of the original ketone is produced to some extent. In this case the first stage is represented by $BuO{\cdot}CR'(CH_2R){\cdot}OMgBr \longrightarrow BuOH + CHR{:}CR'{\cdot}OMgBr$, and in the presence of benzoyl chloride the ester $CHR{:}CR'{\cdot}O_2CPh$ is then formed.

The addition of sodium to ethylenic substances takes place only with those compounds which have aryl groups attached to the carbon atoms concerned in the ethylenic bond. Numerous examples in support of this conclusion are cited by W. Schlenk and E. Bergmann[15] in the course of their lengthy and important communication, comprising more than 350 pages, on the chemistry of the alkali metal-organic compounds. One exception only to this rule has been

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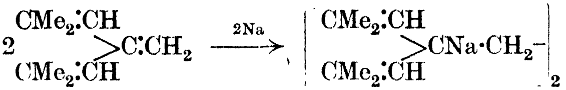
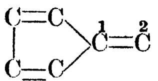
[14] Compare A. Verley, *Bull. Soc. chim.*, 1925, **37**, 537; *A.*, 1925, i, 783; *Ann. Reports*, 1925, **22**, 72; 1927, **24**, 92.

[15] *Annalen*, 1928, **463**, 1; **464**, 1; **A.**, 1031.



$$2\,\begin{matrix}CMe_2{:}CH\\ \\ CMe_2{:}CH\end{matrix}\!>\!C{:}CH_2 \xrightarrow{2Na} \left[\begin{matrix}CMe_2{:}CH\\ \\ CMe_2{:}CH\end{matrix}\!>\!CNa\cdot CH_2-\right]_2$$

(I.)



(II.)

discovered and in this case the substance in question (I) so closely resembles the fulvenes (II) in structure as to render the exceptional behaviour more apparent than real. In general, addition may take place in one of two ways: (*a*) represented by $CPh_2{:}CPh_2 \longrightarrow CPh_2Na{\cdot}CPh_2Na$ or (*b*) represented by $2CPh_2{:}CH_2 + 2Na \longrightarrow CPh_2Na{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_2Na$. In both cases the obvious tendency is for sodium to attach itself only to arylated carbon atoms, and it is interesting to find that in the fulvene series only C_1 combines with sodium [*i.e.*, the reaction follows course (*b*)] unless C_2 is arylated. Lithium enters into additive combination more rapidly than sodium, and sometimes leads to compounds differing in configuration from those derived from the corresponding sodium compounds. For an account of a systematic survey of this problem and of the behaviour of the alkali compounds towards water, carbon dioxide, alkyl halides, and many other reagents, reference must be directed to the original paper.

Carbohydrates.

Monosaccharides and Glucosides.—In studying the optical rotation of sugars in solution Hudson has relied to a considerable extent on the classification of the sugars into α- and β-varieties. This has been subjected to criticism [16] and it is pointed out that contradictory results are obtained when other physical constants are considered. It is necessary to determine more than one additive property and, when only two forms are present during mutarotation, the ratio $k_1/k_2 = K$ must be constant. From observations of specific rotation and molecular volume the value K is 0·50 and 0·47 for mannose, whereas from the index of refraction the value $K = 0{\cdot}64$ is deduced. It is thus concluded that more than two forms of mannose are present in solution, although the α- and β-varieties preponderate. A similar conclusion is also reached from the study of the optical behaviour of galactose [17] in aqueous solution. The mutarotation curves of α-galactose do not obey the unimolecular law, and the early stages of the changes are rapid. With β-galactose there is no change of rotation during 4 minutes, after which time the mutarotation proceeds rapidly, giving an inflected curve with a maximum at about 10 minutes. Assuming the third variety of galactose to be a form μ, the mutarotation is represented by $\alpha\text{-} \rightleftharpoons \mu \rightleftharpoons \beta\text{-}$, and the rotatory power of μ is of the same order as for β-galactose. It is calculated that at equilibrium the proportions of each form present are : α-, 28·5%; β-, 59·5%; μ, 12%.

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[16] C. N. Riiber and J. Minsaas, *Ber.*, 1927, **60**, [*B*], 2402; **A.**, 1928, 47.

[17] G. F. Smith and T. M. Lowry, *J.*, 1928, 666; **A.**, 510.

Almost general unanimity of opinion has been reached in regard to the formulation of simple sugars as pyranoses when these occur as free hexoses or pentoses or in the form of their normal glucosides. C. S. Hudson is exceptional, however, in opposing[18] this view and prefers to represent glucose and its α- and β-glucosides as five-atom ring structures. He included in this category also β-mannose, lyxose, and α-methyl-lyxoside. From optical rotation values, combined with an extension of the additive principle of optical superposition, Hudson has computed rotational effects which are singular in all the above cases. Since they do not yield expected values on the above statistical basis, the above-mentioned sugars and their glucosides are given a five-atom ring structure as distinct from the six-atom ring structure which is conceded for galactose, arabinose, xylose and α-mannose.

In a further reply to this argument other authors[19] have reviewed the statistical method of Hudson and have demonstrated that in its application to the ring-structure of sugars it gives rise to fallacious deductions which are contrary to the chemical facts. It is shown that, whilst Hudson's value *a* (for the rotational effect of that part of a sugar which involves the carbon atom of the reducing group) is approximately a constant for the glucose, galactose, xylose series yet quite another value for the constant is furnished by the series mannose, rhamnose, lyxose. Indeed, if the latter series had been the commoner or more accessible sugars, this singularity would have been credited to the former series and statistical conformity would probably have been conceded to the latter.

It is suggested, however, that the lack of statistical agreement in the two series is associated with the *cis*-configuration of the hydroxyl groups in mannose, rhamnose, and lyxose. The new β-form of lyxose has been isolated, and this is in every respect comparable with β-mannose.

Moreover, as a final argument, α-methyl-lyxoside (I) has been methylated to give the crystalline trimethyl lyxose (II). This yields a δ-lactone (III), which undergoes oxidation to *d*-arabotrimethoxyglutaric acid (IV).[20]

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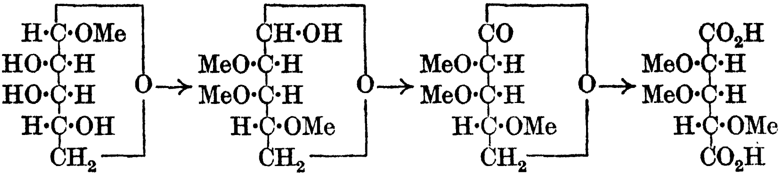
[18] F. P. Phelps and C. S. Hudson, *J. Amer. Chem. Soc.*, 1928, **50**, 2049; **A.**, 991; see also *Ann. Reports*, 1926, **23**, 78.

[19] W. N. Haworth and E. L. Hirst, *J.*, 1928, 1221; **A.**, 740.

[20] E. L. Hirst and J. A. B. Smith, *ibid.*, p. 3147.



(I.) (II.) (III.) (IV.)

Two isomeric triacetyl methyl-lyxosides are known, and from the properties of these it is evident that the normal methyl-lyxoside is a lyxo-pyranoside.[21]

Crystalline β-methylfructoside has long been known and has latterly been recognised as β-methylfructopyranoside. The recent isolation of the crystalline α-form is a matter of interest and importance.[22] The α- and β-methylfructosides are seen to stand in the same relation to each other as α- and β-methylglucosides and all of them are six-atom ring forms or pyranosides. It is very satisfactory that the missing form has now been discovered and that fructose in its general relationships is brought completely into line with other sugars.

The interconversion of α- and β-hexosides has hitherto been possible by digestion with methyl-alcoholic hydrogen chloride. A novel method of some utility is now devised whereby β-forms are converted with facility into α-forms in non-ionising solvents containing stannic chloride.[23] In the presence of titanium tetrachloride, tetra-acetyl β-methylglucoside is smoothly converted into the α-variety; the completely acetylated sugars also undergo a similar change, but this is accompanied by the introduction of chlorine: for example, β-glucose penta-acetate is transformed into α-chloroglucose tetra-acetate. The reaction appears to be a general one.

By the use of a very active form of silver chloride the inversion[24] of α-chloroglucose tetra-acetate to the β-compound occurs in 8—10 minutes. The specific rotation of the latter differs by about 30° from that calculated by Hudson. It is suggested that the principle of optical superposition is not valid in these cases and that Hudson's methods of calculation should not be applied.

The remarkable way in which hydrogen of the hydroxyl groups in sugars may be replaced by thallium when employed as thallous hydroxide has again been illustrated.[25] This reaction is likely to prove of great value in effecting the protection of hydroxyl groups in difficult cases.

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[21] P. A. Levene and M. L. Wolfrom, *J. Biol. Chem.*, 1928, **78**, 525; **A.**, 991.

[22] H. H. Schlubach and G. A. Schröter, *Ber.*, 1928, **61**, [*B*], 1216; **A.**, 873.

[23] E. Pacsu, *ibid.*, pp. 137, 1508; **A.**, 275, 1118.

[24] H. H. Schlubach, P. Stadler, and I. Wolf, *ibid.*, p. 287; **A.**, 398.

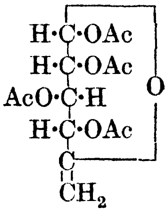
[25] R. C. Menzies and (Miss) M. E. Kieser, *J.*, 1928, 186; **A.**, 275.

By treatment with dilute alkali methylated sugars are shown to undergo the Lobry de Bruyn and von Ekenstein transformation in much the same way as the unsubstituted sugars. For instance, tetramethyl glucose is convertible[26] into tetramethyl mannose, thus confirming the work reported last year on the identity of the ring structure in each of these sugars.

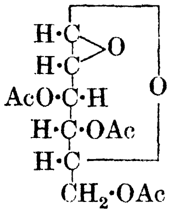
Elimination of phosphoric acid residues in sugars is accomplished by the agency of bone phosphatase. By this procedure the α- and β-methylhexosidediphosphoric acids give rise to α- and β-methylhexosides and it is suggested by the authors that these are recognisable as α- and β-methylfructofuranosides. Thus it would appear that the sugar residue occurring in these compounds is γ-fructose.[27] Deductions based on magnitudes of specific rotation should, however, be accepted with caution, and in the case under review the authors would doubtless be well advised to confirm this important conclusion by applying other and more certain methods of diagnosis.

Compounds having unsaturated sugar chains have long been recognised in the series known as the glucals. A sugar derivative, having an ethylene bond in the side chain of the ring, is now available[28] in the compound α-tetra-acetyl glucoseen (V). The properties of this substance suggest a relationship to the transition products between glucose and lignin or the compound from which lignin arises biologically.

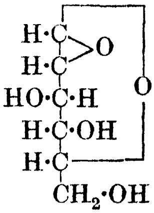
A general study of the use of triacetyl glucose-1 : 2-anhydride (VI) has illustrated the facility with which this reagent[29] combines with hydroxylated compounds with the formation chiefly of β-glucosides.



(V.)



(VI.)



(VII.)

With phenol the reagent yields, however, α-phenylglucoside. A comparison of the properties of the anhydride with those of Pictet's α-glucosan (VII), which should be the parent substance of the above 1 : 2-anhydride, shows a certain disparity, since α-glucosan is said to be capable of crystallisation from methyl alcohol, whereas the substance (VI) combines readily with methyl alcohol to yield the glucoside. The structure allocated to (VI) is, however, supported by the observation that methylation of the glucoside to which it gives rise, followed by elimination of the glucosidic group and of the acetyl residues, leads to the recognition of a 2-methyl glucose. If α-glucosan has the constitution (VII), its properties present some unaccountable difficulties.

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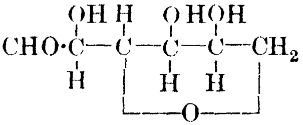
[26] M. L. Wolfrom and W. L. Lewis, *J. Amer. Chem. Soc.*, 1928, **50**, 837; **A.**, 509.

[27] W. T. J. Morgan and R. Robison, *Biochem. J.*, 1928, **22**, 1270; **A.**, 1214.

[28] B. Helferich and E. Himmen, *Ber.*, 1928, **61**, [*B*], 1825; **A.**, 1221.

[29] W. J. Hickinbottom, *J.*, 1928, 3140.

More than usual interest attaches to Fischer and Zach's anhydroglucose, which is recognised as the 3 : 6-glucose anhydride



$$\mathrm{CHO{\cdot}\overset{OH}{\underset{H}{C}}-\underbrace{\overset{H}{C}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH_2}_{O}}$$

and, unlike glucose, has the property of restoring the colour of Schiff's reagent. The constitution here assigned is supported by a new method [30] of preparation of the anhydro-sugar from glucose monoacetone: the latter yields a di-*p*-toluenesulphonyl derivative which, on treatment with 1 mol. of alkali, is converted into a crystalline mono-*p*-toluenesulphonyl derivative of the above. Further treatment with alkali effects the removal of the remaining toluenesulphonyl residue, yielding anhydroglucose-monoacetone, a crystalline substance. Elimination of the acetone residue is brought about by dilute acids and the free anhydro-sugar is then isolated in the crystalline state.

Among several unexpected results is the observation [31] that α-methylmannoside, which is known to have the pyranose structure, is converted into the diacetone compound of α-methylmannofuranoside by the agency of 1% of hydrogen chloride in presence of acetone. It would appear that under these conditions the six-atom ring form is transformed into a five-atom ring form in order to accommodate the two acetone residues which simultaneously condense with the four exposed hydroxyl groups. It is known that this type of change occurs readily in the free sugar, and the α-glucoside form is now seen to respond to the same structural change. The acetone derivatives of xylose have long defied constitutional investigation, and speculation as to the possible occurrence in these compounds of a four-atom ring type of xylose has been current. It is now demonstrated[32] that xylose-monoacetone is a derivative of xylofuranose, since methylation yields a dimethyl derivative which, on hydrolysis and oxidation, passes into a 3 : 5-dimethyl γ-xylonolactone (X). This is converted into the trimethyl γ-xylonolactone (XI) which had previously been identified, and is now shown to yield a crystalline phenylhydrazide. The hydration curves of the lactone and its acid are given and are compared with those from the isomeric trimethyl δ-xylonolactone. Moreover, oxidation of the γ-lactone with nitric acid yielded *d*-dimethoxysuccinic acid.

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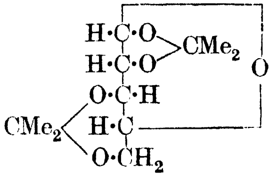
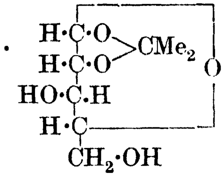
[30] H. Ohle, L. von Vargha, and H. Erlbach, *Ber.*, 1928, **61**, [*B*], 1211; **A.**, 871; K. Freudenberg, H. Toepffer, and C. C. Andersen, *ibid.*, p. 1750; **A.**, 1223. Compare also *ibid.*, pp. 1208, 1870; **A.**, 871, 1220.

[31] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 1928, **78**, 363; **A.**, 992.

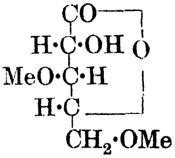
(VIII.)



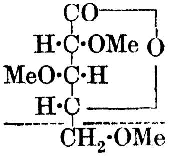
(IX.)



(X.)



(XI.)



It is shown that xylose-monoacetone must have the constitution (IX) and consequently that the diacetone is preferably represented by (VIII).

Di-, Tri-, and Tetra-saccharides.—First in importance among the publications of the year on this topic is the communication by Pictet and Vogel on the synthesis of sucrose. It will be remembered (*Ann. Reports*, 1916, **13**, 90; 1920, **17**, 65) that twelve years ago the advance made in the study of sucrose led to the overthrow of the constitution which had, up to that time, been accepted. Up to 1916 it had been tacitly assumed that, since invert sugar consists of a mixture of glucose and fructose, the forms of the sugars thus isolated were of necessity the forms in which they are combined in the disaccharide. It was then found[33] that methylated sucrose showed no inversion of sign on hydrolysis, and that, whilst the usual form of tetramethyl glucose could be isolated from this product, the methylated ketose displayed a rotatory power and a reaction towards permanganate which at once implied its structural relationship to γ-glucose, and the methylated ketose component was therefore recognised as tetramethyl γ-fructose. Although only a provisional formula could then be allocated, sucrose was thus shown to be a disaccharide in which the normal form of glucose was linked with a γ-form of fructose. It was reported that " a new formula for sucrose is thus indicated which accounts not only for the extreme ease with which the disaccharide is hydrolysed, but also for the previous failure to effect its synthesis." Four years later the isolation of the actual fructose component as a dextrorotatory tetramethyl γ-fructose was announced,[34] and preliminary attempts to ascertain its ring structure were made. At that time all such attempts to elucidate the structure of γ-sugars were doomed to failure so long as the normal sugars were rigidly accepted as butylene-oxide forms. This fallacy underlying the whole of sugar chemistry was exposed and glucose and fructose were shown to have a six-atom ring structure.[35] It was then made abundantly clear that the older formulations of sugars as five-atom ring compounds had been erroneously applied to these substances, and that this discarded formula actually applied to the series of γ-sugars. The six-atom ring sugars, related to pyran, were described as pyranoses: the γ- or five-atom ring sugars were related to furan and designated furanoses.

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[32] W. N. Haworth and C. R. Porter, *J.*, 1928, 611; A., 509.

[33] W. N. Haworth and J. Law, *J.*, 1916, **109**, 1314.

Sucrose was then definitely a complex containing each of the two kinds of sugar ring.[36] The glucose component was present as glucopyranose, and the fructose component as fructofuranose, and in sucrose they were combined by mutual linking through their reducing groups.

It became evident that if a suitably substituted derivative of the dextrorotatory variety of fructose could be prepared (that is, a fructofuranose as distinct from the lævorotatory fructopyranose), a synthesis of sucrose might be attempted with definite prospect of success. After an exhaustive search such a derivative has now been provided in the dextrorotatory tetra-acetyl γ-fructose which occurs as a by-product to the extent of 3% in the preparation of the normal or pyranose form of lævorotatory tetra-acetyl fructose. It is now communicated by Pictet and Vogel[37] that, when this tetra-acetyl γ-fructose (XII) is condensed with tetra-acetyl glucose (XIII) in a chloroform suspension of phosphoric oxide, the genuine octa-acetyl sucrose (XIV) is formed. By the elimination of the acetyl residues the latter substance gives rise to sucrose identical in melting point and optical properties with the natural product.

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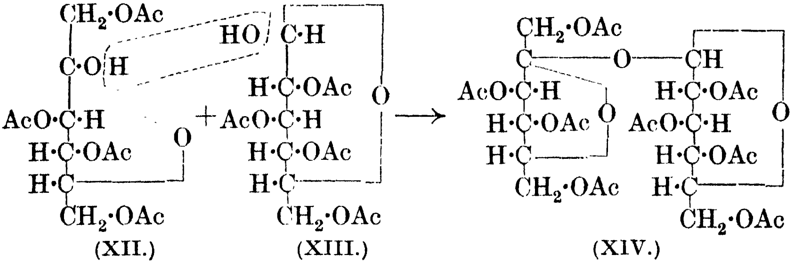
[34] W. N. Haworth, *J.*, 1920, **117**, 199.

[35] *Ann. Reports*, 1925, **22**, 83; 1926, **23**, 74; 1927, **24**, 66.

[36] Avery, Haworth, and Hirst, *J.*, 1927, 2308; **A.**, 1927, 1057.

[37] *Compt. rend.*, 1928, **186**, 724; **A.**, 510; *Helv. Chim. Acta*, 1928, **11**, 436; **A.**, 741.



It appears that sucrose, when crystallised from aqueous methyl alcohol,[38] gives a modification (B), m. p. 171°, whereas from most other organic solvents the sucrose (A) separates, m. p. 185°. All the properties of A and B are identical except the melting point, and the conversion of B into A is instantaneous in water. The differences in the two varieties seem to be purely physical.

In another communication by the same authors [39] an account is given of the condensation of the usual lævorotatory variety of tetra-acetyl fructose with tetra-acetyl glucose, yielding a disaccharide in which both the glucose and the fructose component are pyranose forms. The product, an isomeric form of sucrose described as sucrose C, is crystalline and lævorotatory and differs widely in properties from natural sucrose. It is evident, therefore, that the earlier work on the constitution of natural sucrose is supported by the synthetic experiments of Pictet and Vogel.

The constitution assigned in previous work [40] to melibiose has now been confirmed by a structural synthesis [41] of this disaccharide, which derives its importance from the circumstance that it occurs as an essential component of raffinose. It was noted as a preliminary that α-bromoacetogalactose, when heated with phenol and quinoline, yielded a mixture of α- and β-phenylgalactosides. The formation of this α-galactoside gave promise that, since melibiose has already been assigned an α-configuration, condensation of the above α-bromoacetogalactose (XVI) with 1 : 2 : 3 : 4-tetra-acetyl β-glucose (XV) would yield a mixture of octa-acetyl glucose-α- and -β-galactosides from which octa-acetyl melibiose might be isolated. This has indeed proved to be the case. The octa-acetyl glucose-α-galactoside (XVII) was found to be identical with a specimen of acetylated melibiose.

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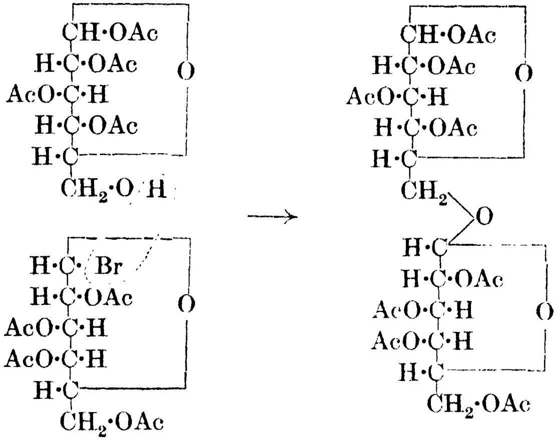
[38] *Compt. rend.*, 1928, **186**, 901; **A.**, 1223.

[39] *Idem, ibid.*, p. 905; **A.**, 1223.

[40] W. N. Haworth, J. V. Loach, and C. W. Long, *J.*, 1927, 3146; **A.**, 1928, 156.

[41] B. Helferich and H. Bredereck, *Annalen*, 1928, **465**, 166.



(XV.) (XVI.) (XVII.)

The application of a similar procedure involving the condensation of (XV) with acetobromoarabinose led to the isolation of a hepta-acetyl derivative of the naturally occurring vicianose. Again, the linking of cellobiose with gentiobiose has been accomplished with the formation of a synthetic tetrasaccharide of definite constitution, although this tetraglucose complex has not been identified with a known natural product.

A method of synthesis of raffinose is reported [42] depending on the fusion of sucrose and galactose, a procedure which is said to give a 1% yield of the trisaccharide. A new tetrasaccharide, which is designated maltotetrose, has also been obtained by condensation of hepta-acetyl maltose, and other new sugars of the trehalose type [43] are obtainable by the similar treatment of β-tetra-acetyl hexoses in toluene containing zinc chloride to which phosphoric oxide is subsequently added.

From the products of fermentation of glucose or fructose, in presence of phosphate, a phosphoric ester of a disaccharide has been isolated. This loses a phosphoric acid residue by the agency of bone phosphatase and liberates trehalose,[44] thus affording a synthesis of this non-reducing disaccharide.

Other disaccharides which are entirely synthetic in origin have been prepared by Freudenberg [45] and his co-workers. They have utilised for this purpose glucose-6-bromohydrin (XVIII). By suitably protecting two hydroxyl residues in this compound, *e.g.*, by an acetone group or two acetyl groups, two hydroxyl positions remain available for condensation, as in the compound (XIX). This has been combined with acetylglucosido-halides of several types, and derivatives of new dihexoses are made available. Other similar experiments have led to the isolation of synthetic trisaccharides of the type (XX).

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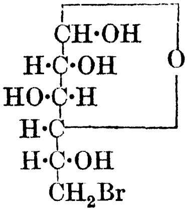
[42] H. Vogel and A. Pictet, *Helv. Chim. Acta*, 1928, **11**, 898; **A.**, 1224.

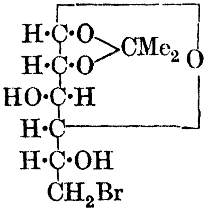
[43] H. Vogel and H. Debrowska-Kurnicka, *ibid.*, p. 910.

[44] R. Robison and W. T. J. Morgan, *Biochem. J.*, 1928, **22**, 1277; **A.**, 1285.

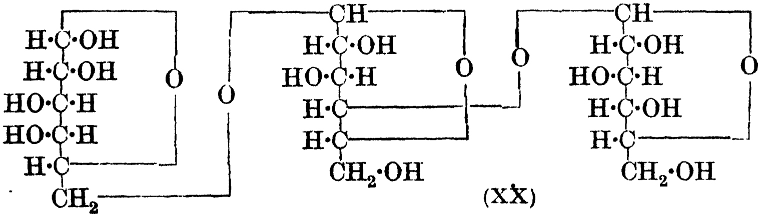
[45] K. Freudenberg, H. Toepffer, and C. C. Andersen, *loc. cit.*; K. Freudenberg, A. Wolf, E. Knopf, and S. H. Zaheer, *Ber.*, 1928, **61**, [*B*], 1743; **A.**, 1222.

(XVIII.)





(XIX.)



(XX)

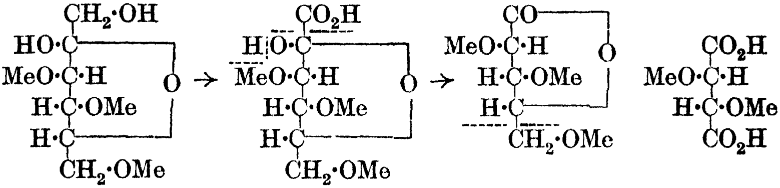
Experiments of great interest and value have also been communicated by the same author [46] dealing with the rates of hydrolysis of disaccharides, glucosides, and sugar-acetones. The figures for the inversion constants of most of the known compounds are thus made available for comparison.

Polysaccharides.—Experiments on the constitution of inulin have revealed [47] the points of junction of contiguous residues of fructofuranose (γ-fructose). Methylation of inulin yielded a "trimethyl inulin," which was hydrolysed to give 3 : 4 : 6-trimethyl fructofuranose (XXI). This yielded a crystalline osazone and underwent oxidation to a 3 : 4 : 6-trimethyl fructuronic acid (XXII). The latter was converted, after methylation, into the same crystalline amide as that which had previously been obtained from tetramethyl fructofuranose derived from sucrose. The presence of the same form of fructose in both sucrose and inulin was thus confirmed. Oxidation of the trimethyl fructuronic acid with acid permanganate led to the isolation of the crystalline *d*-2 : 3 : 5-trimethyl γ-arabono-

[46] K. Freudenberg and others, *Ber.*, 1928, **61**, [*B*], 1735; **A.**, 1222.

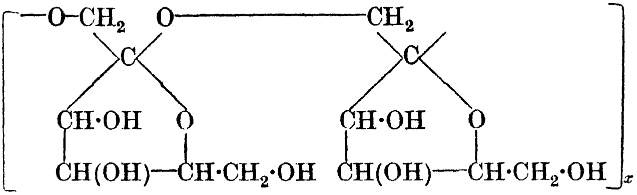
[47] W. N. Haworth and A. Learner, *J.*, 1928, 619; **A.**, 510.

lactone (XXIII). This is characterised by its oxidative degradation to *l*-dimethoxysuccinic acid (XXIV).

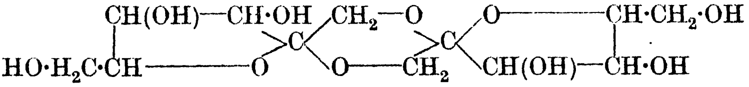


(XXI.) (XXII.) (XXIII.) (XXIV.)

From these results it is shown that the union of the γ-fructose residues in inulin occurs through the positions 1 and 2 in each sugar chain. This structural scheme is indicated below.



On this view, the simplest expression for inulin is the following formula,



wherein two fructose anhydride units are mutually linked. Values for molecular weight determinations of triacetyl inulin have been reported which correspond to hexa-acetyl difructose anhydride, and moreover the complexity of inulin in liquid ammonia is seen to be in agreement with this simple expression. An endeavour to synthesise a compound having this simplified structure has recently been made.[48]

On the other hand, direct determinations of the molecular weight of inulin in water indicate the presence of a more complex molecule, containing at least 24 anhydro-fructose units.[49] Hydrolysis of the inulin in warm water is shown, however, to be progressive and after 28 minutes the above value is diminished to half and the reducing power of the solution increases as the molecular weight diminishes. Under other conditions inulin breaks down readily to give a "lævulin" corresponding to six or eight $C_6H_{10}O_5$ units. Earlier determinations of molecular weight have been commented on in previous Reports. Others are now communicated [50] corresponding to complexes varying from $(C_6H_{10}O_5)_7$ to $(C_6H_{10}O_5)_2$. The former value is obtained by the cryoscopic method with aqueous solutions of inulin. But by heating inulin acetate (at temperatures varying from 250° to 290°) in presence of tetrahydronaphthalene the values diminish progressively to the above minimum. Whether this diminution corresponds to dissociation or decomposition is a problem remaining for future decision.

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[48] H. H. Schlubach and H. Elsner, *Naturwiss.*, 1928, **16**, 772; *Ber.*, 1928, **61**, [*B*], 2358; **A.**, 1221.

[49] H. D. K. Drew and W. N. Haworth, *J.*, 1928, 2690; **A.**, 1360.

Inulin itself, heated with glycerol at 120°/15 mm., is found [51] to undergo definite structural change to a trilævulosan, and at a slightly higher temperature a dilævulosan which reduces Fehling's solution is reported to be the product. It is doubtful, therefore, whether the transformations of inulin acetate already discussed can be interpreted as a simple dissociation or depolymerisation of inulin to its " structural unit."

Recent experiments [52] have shown that the methylation of cellulose at 20° with methyl sulphate gives rise to a trimethyl cellulose which differs essentially from the specimens previously isolated. This is soluble in chloroform, tetrachloroethane, and acetic acid, giving clear viscous solutions, and is quite insoluble in water. The yield is 93% of trimethyl cellulose,[53] and this on hydrolysis furnishes 2 : 3 : 6-trimethyl glucose in a yield of 91%, but in no case could a trace of tetramethyl glucose be isolated. This establishes the structural identity of all the glucose units in cellulose. When it was heated with hydrogen chloride in ether solution, the trimethyl cellulose yielded 1-chloro-2 : 3 : 6-trimethyl glucose, which, in contact with sodium, was transformed into a compound described as 2 : 3 : 6-trimethyl glucose anhydride. According to some earlier theories such a compound would be expected to be the " structural unit " of trimethyl cellulose. But the complete dissimilarity of the anhydride with the latter proves that cellulose cannot be regarded as a unimolecular glucose anhydride. There appeared to be no grounds for the suggestion that trimethyl glucose anhydride would undergo reversible interconversion into trimethyl cellulose. The author thus falls back on the older traditional view that cellobiose is the true breakdown product of cellulose and is not a reversion product. It is held to be probable that cellobiose residues comprise the essential units of cellulose and that these are joined in a chain which is united throughout by ordinary co-valency links. A similar view has also been independently expressed by another worker,[54] and since the cellobiose structure has been finally determined it follows that this picture of the cellulose constitution is given by the scheme :

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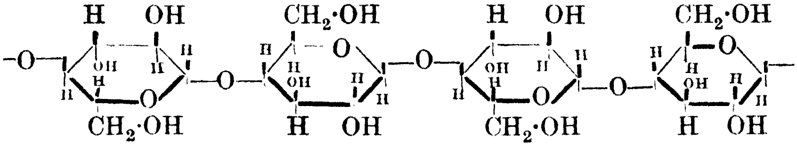
[50] H. Pringsheim and I. Fellner, *Annalen*, 1928, **462**, 231; **A.**, 742; H. Pringsheim and J. Reilly, *Ber.*, 1928, **61**, [*B*], 2018; **A.**, 1225.

[51] H. Vogel and A. Pictet, *Helv. Chim. Acta*, 1928, **11**, 215; **A.**, 276.

[52] H. Urban, *Cellulosechem.*, 1926, **7**, 73; **B.**, 1926, 531.

[53] K. Freudenberg and E. Braun, *Annalen*, 1928, **460**, 288; **A.**, 399; K. Freudenberg, *ibid.*, **461**, 130; **A.**, 743.



A re-interpretation of the crystal lattice of cellulose is held to support this view entirely.[55] The elementary cell has the dimension 10·3 Å. along the fibre axis in ramie cellulose, and the other dimensions of the cell are given as 7·9 and 8·7 Å. This accommodates four glucose residues, and the first dimension is in close agreement with two units of the six-atom ring form of glucose as arranged in cellobiose. It is deduced that the expression formulated above receives strong support, the cellobiose residues being oriented in the direction of the fibre axis and mutually linked by glucosidic oxygen. Forty or more glucopyranose residues are regarded as being joined by β-glucosidic linkings in this way. It is suggested that this structural scheme is in harmony with the established chemical properties of cellulose and is compatible with and affords a ready explanation of the behaviour of cellulose during esterification and swelling.

Other interpretations of the *X*-ray data commented on in last year's Report [56] anticipated in the main these features of the cellulose structure. In one essential detail, however, they differed, inasmuch as the occurrence of the 3·4 Å. line offered difficulties in accepting the cellobiose type of linking of the glucopyranose units. Instead of the union being 1 : 4—1 : 4 between contiguous glucose residues, the earlier authors preferred to arrange the linkings in the order 1 : 4—4 : 1. But the ordered linking of glucopyranose units in long chains arranged side by side is the main conclusion of both interpretations of the *X*-ray diagrams of cellulose. Doubtless these differences will be adjusted by further experimental work, which should be largely chemical in its scope.

The experiments and conclusions of Hess [57] are entirely opposed to these conceptions of the cellulose structure. This author considers that the above interpretations of the *X*-ray diagrams are invalid in so far as they assume the presence of cellobiose residues or of glucosidic disaccharide linkings. He urges that the disentanglement of the structural factors of cellulose in the *X*-ray diagram is rendered difficult by ignorance of the corresponding diagrams of carbohydrates of known structure. The diagrams of a number of such products are now given, and it is claimed that one of these, a biosan ($C_{12}H_{20}O_{10}$) which the author has isolated from cellulose, differs but little from cellulose in the mass distribution of its constituent atoms. The effect of substitution of groups on mass distribution is intimately considered. On this view a more appropriate conception of the cellulose structure is that of an arrangement of masses of the biosan or glucosan complex united by directed associative forces.

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[54] W. N. Haworth, *Helv. Chim. Acta*, 1928, **11**, 534.

[55] K. H. Meyer and H. Mark, *Ber.*, 1928, **61**, [*B*], 593, 1936; **A.**, 621; *Z. angew. Chem.*, 1928, **34**, 935.

[56] *Ann. Reports*, 1927, **24**, 82.

[57] K. Hess and C. Trogus, *Ber.*, 1928, **61**, [*B*], 1982.

In the past, difficulty has been encountered in the preparation of triacetyl and trimethyl starch. Small yields of products were obtained, in some cases after very prolonged and repeated treatments with the substituting agents. This led to serious doubts whether the final products were genuine derivatives of the original starch or of a portion only of the polysaccharide which had been segregated during these observations.

In a new series of experiments [58] starch has been brought into a condition in which it is more susceptible to reagents. Starch paste was quantitatively precipitated with alcohol and gave a powder which retained the properties of the substance. On acetylation this gave a 96% yield of a triacetyl starch. De-acetylation furnished a product having the properties of regenerated amylose. Methylation of the triacetyl starch under new conditions gave rise to a trimethyl starch in 89% yield after only six treatments with the reagents. This is compared with the results of earlier workers, who obtained a 25% yield after 24 methylations. It is shown that a high yield of 2 : 3 : 6-trimethyl glucose was obtainable from the methylated starch. The authors were unable to confirm earlier claims that starch undergoes preferential methylation to a homogeneous dimethyl starch, and the structural views based on such an observation are rendered doubtful. The probability that starch is largely composed of conjugated α-glucopyranose units is discussed and alternative formulæ are considered.

W. N. Haworth.
E. L. Hirst.

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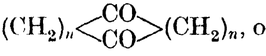
[58] **W. N. Haworth, E. L. Hirst, and J. I. Webb, *J.*, 1928, 2681; A., 1360.**

PART II.—HOMOCYCLIC DIVISION.

IN this contribution the aim will be to bring up to date the account of those subjects which, having been discussed in one or more of the corresponding Reports since 1923, have subsequently made marked progress. Other topics will be left aside that they may be dealt with by a future Reporter in a more connected manner than would be possible if they were discussed at the present stage.

Large Carbon Rings.

(Continued from *Ann. Reports*, 1926, **23**, 112—119.)

Since the date of the Report referred to, a detailed examination by Ruzicka and his collaborators of the distillates obtained from thorium azelate and sebacate, from yttrium nonane- and decane-$\alpha\omega$-dicarboxylate, from thorium pentadecane-, octadecane-, and nonadecane-$\alpha\omega$-dicarboxylate, and from yttrium eicosane- and octacosane-$\alpha\omega$-dicarboxylate, has led to the isolation of a large number of new cyclic and open-chain compounds. The cyclic substances include hydrocarbons with rings of 16, 18, and 30 methylene groups, monoketones with rings containing 19, 20, 21, 29, and 30 carbon atoms, and a series of symmetrical cyclic diketones with 16, 18, 20, 22, and 30 carbon atoms in their rings. The last group of substances are of the type  $(CH_2)_n{<}{\substack{CO\\CO}}{>}(CH_2)_n$, of which the only previously known examples are the *cyclo*butane- and *cyclo*hexane-diones.

The following table contains a list, complete from C_{15} to C_{30}, of the saturated, unbranched, cyclic hydrocarbons, monoketones, and diketones which have been described up to the time of writing. The figures represent the m. p.'s of the compounds; those in Roman type relate to compounds the preparation of which is referred to in the Report for 1926, and those in italics to those which have been prepared since that time.

	C_{15}.	C_{16}.	C_{17}.	C_{18}.	C_{19}.	C_{20}.	C_{21}.	C_{22}.	. . .	C_{29}.	C_{30}.
Hydrocarbons	61°	*61°*	75°	*72°*	—	—	—	—	. . .	—	*54°*
Monoketones	63	56	63	71	*72°*	*59°*	*46°*	—	. . .	*47°*	*Not taken
Diketones	—	*84*	—	*97*	—	*51*	—	*56°*	. . .	—	*75*

* Semicarbazone, m. p. *150°*.

For convenience in formulation, $(CH_2)_n$ will now be replaced by C_n, and a number in heavy type will be used to indicate the total number of carbon atoms in each ring.

($CO_2H{\cdot}C_7{\cdot}CO_2H$). Two new ketones have been isolated from the distillate from thorium azelate, namely, *cyclo*hexadecane-1 : 8-dione and $\alpha\omega$-di-*n*-octoyl-*n*-heptane.[1] The course of the decomposition may therefore be represented as follows:

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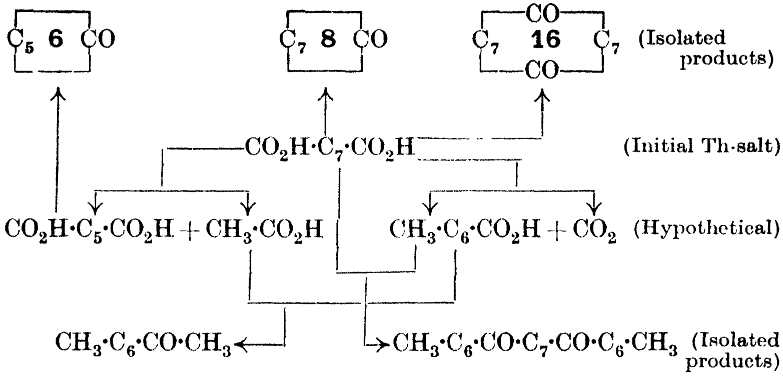
[1] L. Ruzicka, W. Brugger, C. F. Seidel, and H. Schinz, *Helv. Chim. Acta*, **1928, 11, 496**; **A.**, 642.



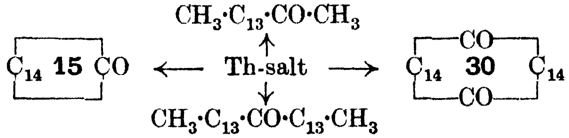
The C_{16}-diketone was obtained in 1% yield, and was converted by reduction by Clemmensen's method into the known C_{16}-monoketone and the new C_{16}-hydrocarbon.

($CO_2H{\cdot}C_8{\cdot}CO_2H$). The identified ketones from the distillate from thorium sebacate correspond precisely with those from thorium azelate, excepting that the open-chain diketone of the series was not isolated. The new product is the cyclic C_{18}-diketone, which on reduction yielded the new C_{18}-hydrocarbon.[2]

($CO_2H{\cdot}C_9{\cdot}CO_2H$). Distillation of the yttrium salt of nonanedicarboxylic acid yielded,[3] in addition to the cyclic C_{10}-ketone previously obtained from the corresponding thorium salt, a cyclic C_{20}-diketone, from which a C_{20}-monoketone was obtained by reduction.

($CO_2H{\cdot}C_{10}{\cdot}CO_2H$). Distillation of yttrium decanedicarboxylate gave,[4] not only the cyclic C_{11}-ketone previously obtained from the thorium salt, but also the cyclic C_{22}-diketone and methyl decyl ketone.

($CO_2H{\cdot}C_{14}{\cdot}CO_2H$). Three new ketones have been isolated [5] from the by-products obtained in the manufacture of " exaltone " from thorium tetradecanedicarboxylate, namely, methyl tetradecyl ketone, ditetradecyl ketone, and *cyclo*triacontanedione. The last was reduced to *cyclo*triacontanone and *cyclo*triacontane :



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[2] L. Ruzicka, W. Brugger, C. F. Seidel, and H. Schinz, *Helv. Chim. Acta*, 1928, **11**, 496 ; **A.**, 642.

[3] L. Ruzicka, M. Stoll, and H. Schinz, *ibid.*, p. 670; **A.**, 887.

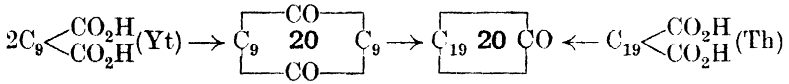
[4] *Idem, ibid.*

[5] L. Ruzicka, W. Brugger, C. F. Seidel, and H. Schinz, *loc. cit.*

The formation of the open-chain ketones can obviously be explained along the lines indicated in the case of the products from thorium azelate.

$(CO_2H{\cdot}C_{18}{\cdot}CO_2H)$. *cyclo*Nonadecanone[6] was obtained in 2·5% yield from the thorium salt of octadecanedicarboxylic acid.

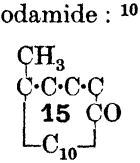
$(CO_2H{\cdot}C_{19}{\cdot}CO_2H)$. The odd acids of the normal dibasic series are naturally not easily obtainable by Walker's electrolytic synthesis, but japanic acid, a product of the hydrolysis of Japan wax, was proved by a somewhat complex synthesis (not suitable for preparative purposes) to be nonadecane-αω-dicarboxylic acid. A convenient natural source of this acid thus being available, it was prepared in quantity sufficient for conversion by distillation of its thorium salt into *cyclo*eicosanone, identical with the monoketone obtained by reduction of the cyclic diketone from nonanedicarboxylic acid.[7]



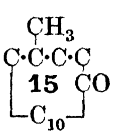
$(CO_2H{\cdot}C_{20}{\cdot}CO_2H)$. Distillation of the yttrium salt of eicosane-αω-dicarboxylic acid gave the cyclic C_{21}-monoketone in nearly 4% yield.[8]

$(CO_2H{\cdot}C_{28}{\cdot}CO_2H)$. *cyclo*Nonacosanone was obtained in rather more than 1% yield from yttrium octacosane-αω-dicarboxylate.[9]

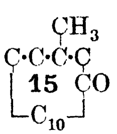
Analogues of Muscone.—Muscone was originally identified as β-methylexaltone, although the evidence of its constitution left a certain doubt as to whether it might not be the γ- or δ-methyl isomeride. The last two compounds have now been prepared by distillation of the appropriate thorium salts, and α-methylexaltone by direct methylation of exaltone with methyl iodide and sodamide:[10]



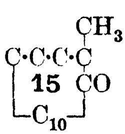
(From Th and Yt salt)



(From Th salt)



(Muscone)



(From exaltone)

γ-Methyl*cyclo*tetradecanone has also been prepared by yttrium salt distillation, and α-methyl*cyclo*heptadecanone by methylation of dihydrocivetone.[11]

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[6] L. Ruzicka, M. Stoll, and H. Schinz, *loc. cit.*, p. 1174; **A.**, 1929, 68.

[7] *Idem, ibid.*, p. 670; **A.**, 887.

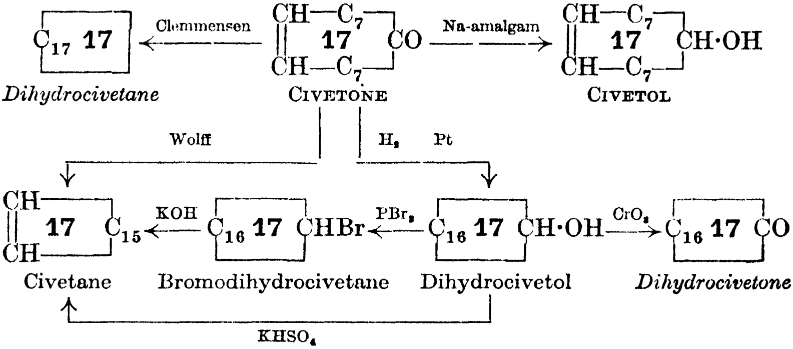
[8] *Idem, ibid.*, p. 1174; **A.**, 1929, 68.

[9] *Idem, ibid.*

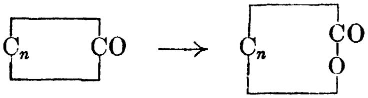
[10] L. Ruzicka, H. Schinz, and M. Pfeiffer, *ibid.*, p. 686; **A.**, 887.

[11] *Idem, ibid.*

Analogues of Civetone.—Natural civet contains, in addition to civetone, about 3% of civetol, which has also been prepared by reduction of civetone. The present condition of the chemistry of *cyclo*heptadecane derivatives is indicated [12] in the following scheme, in which capitals are used for natural products and italics for those derivatives which have been independently synthesised from hexadecanedicarboxylic acid :



Analogues of Vegetable Musks.—A number of the above cyclic ketones have been oxidised by Caro's acid to large-ring lactones identical with, or allied to, the vegetable musks : [13]



Optical Activity dependent on Restricted Rotation.

(Continued from *Ann. Reports*, 1926, **23**, 119—126.)

This subject had its birth in the chemistry of diphenyl derivatives and the position as it appeared at the end of 1926 may be summarised as follows. Of the three types of observations which had been considered to receive explanation by means of Kaufler's folded diphenyl formula (I), namely,

(*a*) the formation of rings of type (II),
(*b*) the existence of geometrical isomerides of type (III),
(*c*) the optical resolution of derivatives of type (IV),

the whole of the evidence summarised under (*a*) had been proved incorrect, most, but not quite the whole, of that referred to under (*b*) had also been shown to be incorrect, and the whole of that referred to under (*c*) had received an alternative explanation.

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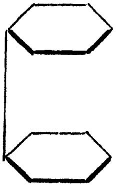
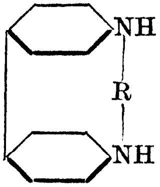
[12] L. Ruzicka, H. Schink, and C. F. Seidel, *loc. cit.*, 1927, **10**, 695; **A.**, 1927, 1189.

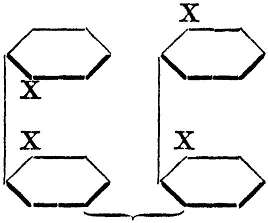
[13] L. Ruzicka and M. Stoll, *ibid.*, 1928, **11**, 1159; **A.**, 1929, 67. Compare M. Kerschbaum, *Ber.*, 1927, **60**, [*B*], 902; **A.**, 1927, 541.



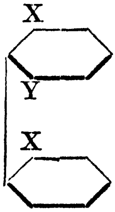
(I.)



(II.)



(III.)

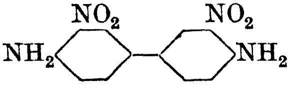


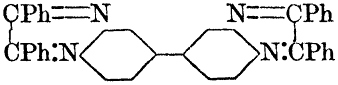
(IV.)

Since 1926 the work of destruction has been completed; further, the new theory has been placed on a firmer foundation.

The Kaufler Theory.—Two points regarding the alleged geometrical isomerides remained to be cleared up. The first concerned Le Fèvre and Turner's proof that one of Cain's supposed stereoisomeric 3 : 3′-dinitrobenzidines (V) was really the 2 : 3′-derivative (VII). The difficulty here was that Cain had reduced both his isomerides to the corresponding tetra-aminodiphenyls, from which he had obtained the same quinoxaline (VI) on treatment with benzil;

(V.)

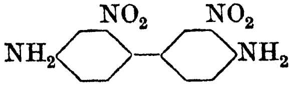


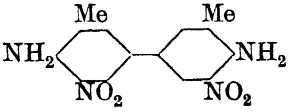


(VI.)

further, O. L. Brady and G. P. McHugh[14] had recorded confirmation of this result. The explanation[15] is that the 2 : 3′-derivative handled by these workers was impure, containing about 2—3% of the 3 : 3′-isomeride, and it therefore did give a trace of the quinoxaline (VI). As it had been omitted to mention the yield, this explanation of the difficulty had remained unsuspected.

(VII.)

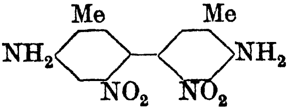


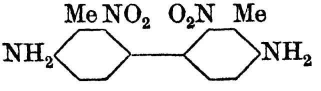


(VIII.)

The second point concerned Cain's alleged isolation of each of the three dinitrotolidines (VIII), (IX), and (X) in *cis*- and *trans*-forms.

(IX.)





(X.)

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[14] *J.*, 1923, **123**, 2047.

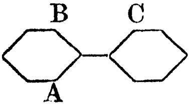
[15] R. J. W. Le Fèvre, D. D. Moir, and E. E. Turner, *J.* 1927, 2330; **A.**, 1927, 1062.

It is now clear, however,[16] that those which are not position isomerides are mixtures.

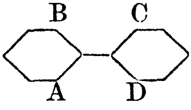
Finally, not only does no relic of the evidence previously supposed to support the Kaufler formula now survive, but also the formula itself has been definitely disproved in the following way :

If the Kaufler conception be correct, then a 4 : 4′-disubstituted diphenyl, with two identical substituents circularly symmetrical about the bonds uniting them to the aromatic nuclei, should possess a molecular electric moment parallel to the intersection of the two planes of molecular symmetry. It is not necessary that the rings should be *parallel* to produce this result : any angle other than 180° between the planes of the rings will correspond with a definite dipole moment in the 4 : 4′-derivative. Its value will, indeed, approximate to $2\mu \cos \theta/2$, where μ is the individual moment of each substituted phenyl group ; and this expression vanishes only if $\theta = 180°$, that is, if the rings are co-axial. 4 : 4′-Dichlorodiphenyl fulfils the necessary geometrical requirements, and for small values of θ (Kaufler's theory) its electric moment should be large, since that of chlorobenzene is large ; actually it is zero.[17]

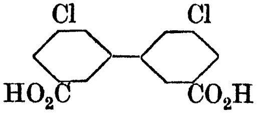
The Theory of Restricted Rotation.—This view, which was advanced almost simultaneously in slightly different forms by Turner and Le Fèvre, Bell and Kenyon, and Mills, in order to account for the optical resolution of certain diphenyl derivatives, assumes that whilst the rings are, or may be, coaxial, their rotation is restricted in certain *substituted* diphenyls by the interaction of the substituents, which thus prevent the rings from becoming coplanar. The nature of the forces which give rise to this result is a question on which opinions differed, but leaving this aside, one immediately obvious merit of the theory was that it explained why all the known optically active diphenyl derivatives possessed at least three ortho-substituents (types XI and XII) : for only *o*-substituents (*e.g.*, 2 : 2′, 2 : 6′) would be expected to be close enough to one another to give rise to the postulated restrictive forces by mutual interaction ; and three such substituents might be necessary to stop *both* the ways in which one ring might attain the plane of the other during a complete rotation :



(XI.)



(XII.)



(XVI.)

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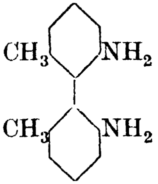
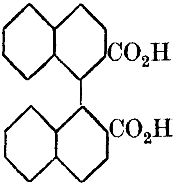
[16] R. J. W. Le Fèvre and E. E. Turner, *J.*, 1928, 963 ; **A.**, 630.

[17] J. W. Williams and A. Weissberger, *J. Amer. Chem. Soc.*, 1928, **50**, 2332 ; **A.**, 1180.

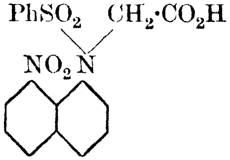
Since this theory was advanced the following additional compounds of types (XI) and (XII) have been obtained in optically active forms: 6 : 6′-diamino-*o*-ditolyl[18] (XIII) and 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid[19] (XIV). Furthermore, the following additional compounds, each with an insufficient number of ortho-groups, have been investigated with the object of resolving them, and have resisted resolution: 4-nitrodiphenyl-2′ : 3-dicarboxylic acid,[20] 4 : 4′-dinitrodiphenic acid,[20] and 5 : 5′-dichlorodiphenyl-3 : 3′-dicarboxylic acid[21] (XVI).



(XIII.)



(XIV.)



(XV.)

All these additional examples naturally give further support to the theory, but it is evident that the most satisfactory way of demonstrating the nature of the phenomenon under observation is to carry it outside the diphenyl series altogether, and this has been done by W. H. Mills and K. A. C. Elliott in the example of the *peri*-naphthalene derivative (XV). Here the theory suggests that the free rotation of the benzenesulphonylglycine residue should be restricted by the *peri*-nitro-group; and the compound was, in fact, resolved,[22] although its optical stability proved to be rather slight.

With regard to the nature of the forces which inhibit free rotation it is still difficult to form a definite view. Mills considered that mere mechanical obstruction was a sufficient explanation, provided that the requisite molecular rigidity could be presumed. Turner, Kenyon, and their associates left open the question whether electropolar forces might not also be responsible, and this seems to be the wiser course, although the simplicity of Mills's suggestion is attractive. If mechanical obstruction were the sole obstacle to rotation, it would be expected that the optical stability of analogous compounds should diminish with the size of the obstructing substituents independently of their electro-chemical nature, and although no comparative measurements on these lines have yet been instituted, Meisenheimer's diaminoditolyls (XIII) are not at all prone to racemisation, notwithstanding that, at most, a very slight distortion of the molecule should enable the relatively small substituents present in these compounds to pass one another. The introduction of a fourth *o*-substituent into a diphenyl compound already containing three (XVII), (XVIII), certainly does enhance the optical stability,[23] but this would be expected on any view as to the nature of the obstructing forces :

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[18] J. Meisenheimer, *Ber.*, 1927, **60**, [*B*], 1245; **A.**, 1927, 766. This author, apparently unaware that he had been anticipated, also advanced the theory of restricted rotation by the interaction of substituents. The abstract cited reproduces the theory, but makes no mention of the fact that it was not new.

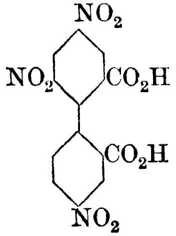
[19] R. Kuhn and O. Albrecht, *Annalen*, 1928, **465**, 282; **A.**, 1242.

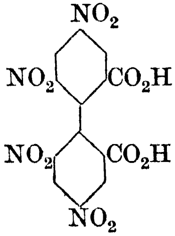
[20] *Idem*, *ibid.*, 1927, **455**, 272; **A.**, 1927, 876.

[21] F. B. McAllister and J. Kenner, *J.*, 1928, 1913; **A.**, 1006.

[22] *J.*, 1928, 1291; **A.**, 748.

(XVII.)
(Racemised)





(XVIII.)
(Not racemised)

*Tautomerism.**

(Continued from *Ann. Reports*, 1927, **24**, 106—119.)

(I) *Prototropy.*—In last year's account of this subject the principal place was given to the results and interpretation of Kon and Linstead's extensive work on the effect of substituents on the behaviour of the pentad systems represented by αβ- and βγ-unsaturated carbonyl and cyano-compounds. It is necessary briefly to refer to this subject again, because, although the effect of substitution of carboxyl and similar groups for hydrogen in the α-, β-, and γ-positions, and of alkyl groups in the β- and γ-positions, was discussed, no example illustrating the remaining case, namely, the influence of an α-alkyl group, had then been quantitatively studied.

It will be recalled that the effect of γ-substitution of a methyl group for hydrogen was to displace the equilibrium in the direction of the βγ-form : the interpretation was that the substituent would charge the γ-carbon atom slightly negatively ($+ I$ effect) and thus decrease its toleration for the negative ionic charge which has to be distributed between the α- and γ-carbon atoms (and the carbonyl group) when the mobile proton has left the system. An α-methyl group would be expected to act oppositely, for a corresponding reason.

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* This section includes two short articles, Ic, and IId, on the *pinacol–pinacolin, Wagner, and allied rearrangements*, the subject being continued from *Ann. Reports*, 1924, **21**, 96; 1925, **22**, 115.

[23] R. Kuhn and O. Albrecht, *Annalen*, 1927, **458**, 221; **A.**, **1928**, **63**.

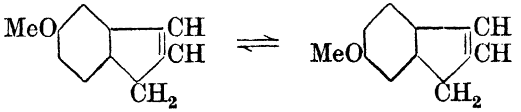
This year A. A. Goldberg and R. P. Linstead, using Linstead's quantitative technique, have not only given a further striking illustration of the influence of the γ-methyl group, but have also furnished the first instance showing the opposite effect of an α-methyl substituent.[24] The new data relate to the anions of pentenoic acid and its α- and γ-methyl derivatives, and are as follows :

γ-Methyl acids.	Pentenoic acids.	α-Methyl acids.
(αβ-, 5·6%)	(αβ-, 75·4%)	(αβ-, 80·7%)

The branches of the subject now to be reviewed relate to the prototropy of triad systems, ring-chain systems, and pinacolic systems, respectively.

(a) *Triad systems.* The one established case of a three-carbon triad system which exhibits mobility under ordinary conditions is that of 5-methoxyindene, although, of course, indene and its substitution products generally are involved by implication. Briefly stated, the evidence with regard to the methoxyindene is that when it is prepared by methods calculated to yield the isomerides (I) and (II), the same compound results, which in its chemical behaviour combines the properties to be expected from the two isomerides : [25]

(I.)



(II.)

It had been suggested [26] that the high degree of mobility thus indicated was connected with the stability of the metallic derivatives of indene, that is, of the potential indenyl anion, but the theoretical problem of accounting for this stability was left unsolved. Now, however, the suggestion has been made [27] that it should be referred back to the view that aromatic systems in general owe their stability to the formation of a highly stable sextuple valency group. This theory was first advanced by E. Bamberger,[28] whose arguments are simple and convincing : pyrroles are exceptionally weak bases and this is because the salt-forming valencies of the nitrogen atom (in modern terminology, the unshared electrons) are required to form the sextuple group; pyridines, on the other hand, are relatively strong bases, because the sextuple group can be formed without calling on the latent valencies of the nitrogen atom, which therefore remain available for salt formation. This is only one of many examples adduced by Bamberger. Without assumption as to the precise location of the stable group, the conception may be expressed by (III) and (IV), where each arrow represents a contributing duplet. Benzene (V) is obviously in the same case as pyridine in regard to its ability to provide the electrons for the stable sextet, but *cyclo*pentadiene can do so only by the appropriation of the electrons of one of its hydrogen atoms, which thus becomes ionisable; it is this circumstance which gives to the hydrocarbon and its derivatives properties analogous to those of an acid (VI), and confers stability on the corresponding anion (VII) :

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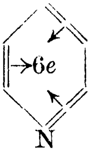
[24] *J.*, 1928, 2343; **A.**, 1214.

[25] C. K. Ingold and H. A. Piggott, *J.*, 1923, **123**, 1469.

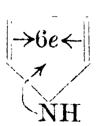
[26] *Idem*, *ibid.*, and *J.*, 1922, **121**, 2381.

[27] F. R. Goss and C. K. Ingold, *J.*, 1928, 1268; **A.**, 758.

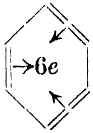
[28] *Ber.*, 1891, **24**, 1758; *A.*, 1891, 1090; *Ber.*, 1893, **26**, 1946; *A.*, 1893, 727; *Annalen*, 1893, **273**, 373; *A.*, 1893, 426.



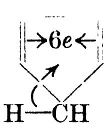
(III.)



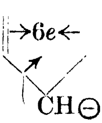
(IV.)



(V.)

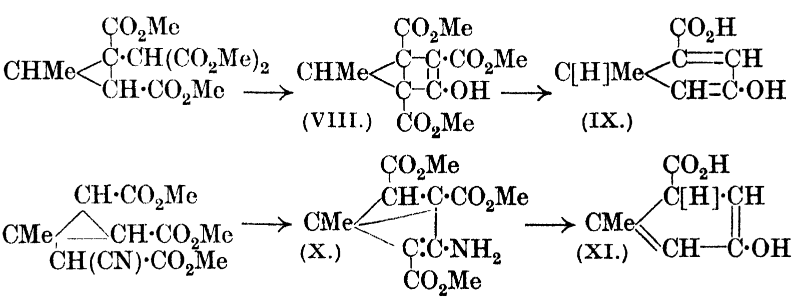


(VI.)



(VII.)

The above applies, of course, not only to *cyclo*pentadiene but also to indene and fluorene, but owing to the formal three-carbon triad systems present in the former two, the anionic charge, once produced, will tend to distribution—between all five nuclear carbon atoms in the case of *cyclo*pentadiene, and between the 1- and 3-positions in the case of indene, and these positions represent the possible points of reunion of the ionised proton. Evidence of the prototropic mobility which should characterise the nucleus of *cyclo*pentadiene is not so complete as in the case of indene, but is indicated, both by the identity of the acids (IX) and (XI) prepared according to the schemes formulated below, and also by mild oxidation of the crystalline intermediate (X) (VIII is an oil), which yielded products indicative of both types of structure :[29]



Several examples are known of open-chain three-carbon systems terminated by phenyl groups, and of these the simplest is the conversion of allylbenzene into the isomeric propenylbenzene.[30] This reaction and those analogous to it require catalysis by hydroxide or ethoxide ions in considerable concentration at a high temperature, and the same holds true even when two aryl groups are present, one at each end of the three-carbon system.[31] A comparison of the latter case with that of indene, in which also the three-carbon system is terminated at both ends by an aryl residue, shows the reduction of mobility which accompanies the loss of the driving mechanism, depending, if the above suggestion be correct, on Bamberger's principle.

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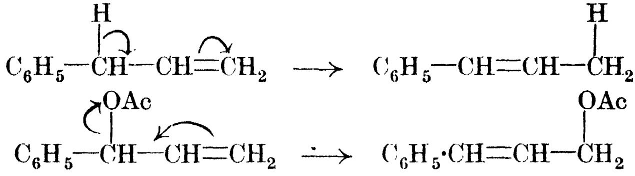
[29] F. R. Goss and C. K. Ingold, *loc. cit.*

As to the effect of aryl groups on equilibrium, the conversion of allylbenzene into propenylbenzene is nearly or entirely complete; and for the purpose of considering how the phenyl group brings about this result, it should be considered in conjunction with the also substantially complete *anionotropic* conversion (see below) of α-phenylallyl esters into cinnamyl esters : [32]



$$C_6H_5{-}\overset{H}{C}H{-}CH{=}CH_2 \longrightarrow C_6H_5{-}CH{=}CH{-}\overset{H}{C}H_2$$

$$C_6H_5{-}\overset{OAc}{C}H{-}CH{=}CH_2 \longrightarrow C_6H_5{\cdot}CH{=}CH{-}\overset{OAc}{C}H_2$$

Probably the most satisfactory conception of the polar behaviour of the phenyl group (although the theoretical problem here involved is one of some difficulty) is that its main effect is a tautomeric one of either sign ($\pm T$), and that it therefore acts by attracting or releasing electrons according to the *momentary* requirements of the attacking reagent; [33] for a general consideration of side-chain reactivity in aromatic compounds shows that the phenyl group facilitates, not only side-chain reactions which involve the separation of shared electrons, but also those requiring their retention. In the cases under consideration, the attacking reagent is the catalyst or solvent molecule the electric field of which assists the removal of the mobile kation or anion. The phenyl group probably first facilitates the ionisation, and then absorbs part of the charge thus produced on the α-carbon atom, leaving the γ-carbon atom to receive the detached ion.

The influence of a *p*-methoxyphenyl group is interesting. The polar properties of the methoxyl group comprise [33] a somewhat weak inductive electron-attraction, and a very powerful tendency towards tautomeric electron-release. But the tautomeric effect happens to be of the wrong sign to absorb the charge produced in *prototropic* change (not anionotropic change, however—see later). Therefore the inductive effect takes control; and thus the methoxyl group assists its aromatic residue. This is illustrated by the proportion of the isomerides in the following equilibrium [34] which is established in alcoholic sodium ethoxide at 85° :

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[30] M. Tiffeneau, *Compt. rend.*, 1904, **139**, 482; *A.*, 1904, i, 872; M. Ageewa, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 664; *A.*, 1905, i, 776; A. Klages, *Ber.*, 1906, **39**, 2590; *A.*, 1906, i, 661.

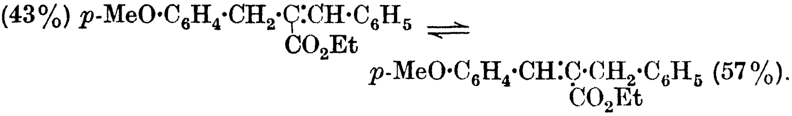
[31] C. W. Shoppee, *J.*, 1928, 2567; **A.**, 1240.

[32] H. Burton and C. K. Ingold, *ibid.*, p. 904; **A.**, 634; H. Burton, *ibid.*, p. 1650; **A.**, 880.

[33] *Ann. Reports*, 1927, **24**, 151. In lines 7 and 6 from bottom the arrows should be interchanged.

$$(30\%)\ p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot CH{:}CH\cdot C_6H_5 \rightleftharpoons p\text{-MeO}\cdot C_6H_4\cdot CH{:}CH\cdot CH_2\cdot C_6H_5\ (70\%).$$

When, in addition, a group such as carbethoxyl, the inductive effect of which is of the same sign as that of methoxyl, is introduced into a position such that the group should affect both terminal atoms of the system equally, the inequality in the proportion of the isomerides is still in the same direction, but, naturally, the disparity between the figures is less : [34]



$$(43\%)\ p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot \underset{CO_2Et}{C}{:}CH\cdot C_6H_5 \rightleftharpoons p\text{-MeO}\cdot C_6H_4\cdot CH{:}\underset{CO_2Et}{C}\cdot CH_2\cdot C_6H_5\ (57\%).$$

Very little is at present known with regard to the open-chain " methyleneazomethine " triad system, $\cdot CH{:}N\cdot C\cdot$, and attempts to prepare *iso*indole have not so far been successful.[35] Indeed, the Reporter's acquaintance with the literature includes no clear case of mobility in any system of this type. Nevertheless, mobility in this system has been realised, and appears [34] (as was foreshadowed [36] from theoretical considerations advanced in 1922) to be of about the same order as the mobility of the three-carbon triad system. It is probable, moreover, that the effect of substituents on the equilibrium will be found to be governed by similar laws for both these systems. Thus, under conditions similar to those described for the methoxyhydrocarbons, the methoxy-azomethines, $p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot N{:}CH\cdot C_6H_5$ and $p\text{-MeO}\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_5$, attain a similar equilibrium, although the disparity between the proportions is somewhat greater.[34]

(b) *Ring-chain systems.* The use of aromatic nitrogen sugars has enabled new light to be thrown on the ring-chain prototropic changes which underlie [37] the mutarotation of sugars generally. Since the recognition of the essential character of these changes, theories regarding them have developed along two main lines.

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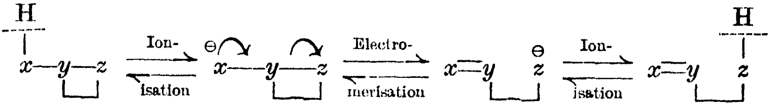
[34] C. K. Ingold and C. W. Shoppee, unpublished observations.

[35] G. W. Fenton and C. K. Ingold, *J.*, 1928, 3295.

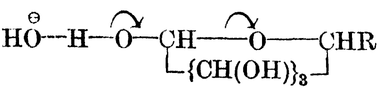
[36] C. K. Ingold and H. A. Piggott, *J.*, 1922, **121**, 2383.

[37] J. W. Baker, C. K. Ingold, and J. F. Thorpe, *J.*, 1924, **125**, 268; *A.*, 1924, i, 262; R. Kuhn and P. Jacob, *Z. physikal. Chem.*, 1924, **113**, 389; *A.*, 1925, ii, 49.

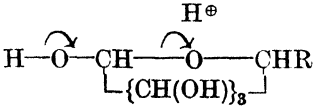
C. K. Ingold, C. W. Shoppee, and J. F. Thorpe[38] examined the effect of structural influences on prototropy on the basis of a mechanism which, in its application to ring-chain prototropy, would be formulated thus :



the assumed function of catalysts being the facilitation of the primary ionisation. According to J. W. Baker,[39] catalysts may be of two kinds : (1) those which externally attract the ionising proton directly (bases and the anions of weak acids); (2) those which facilitate its liberation indirectly by increasing the internal attraction on its shared electrons (acids and the anions of weak bases). Formulæ (XII) and (XIII) illustrate the two mechanisms :

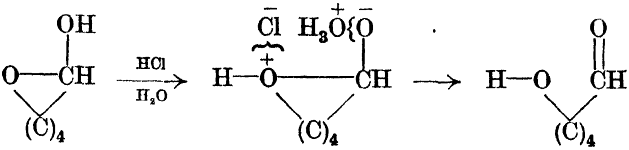


(XII.)



(XIII.)

T. M. Lowry,[40] on the other hand, has developed a conception of prototropy in relation to mutarotation, in which it is considered that *two* catalytic molecules (or ions) simultaneously attack the sugar molecule at the points corresponding to x and z. One acts as a proton-donator and the other as a proton-acceptor, and the result is to produce a bipolar ion, which undergoes internal neutralisation with a change of structure. Taking as example the simultaneous attack of an acid and water, the theory may be expressed as follows :



In order to arrive at a decision between this theory of duplex catalytic action and the unitary theory, J. W. Baker[41] introduced the consideration that if the ·OH group in the cyclol form is replaced by ·NH·C_6H_4R and R is varied, then, according to the duplex mechanism, the facility of the change should depend on the extent to which R collaborates with the proton-acceptor; that is, the relative velocities should run parallel with the relative strengths of the acids, $R{\cdot}C_6H_4{\cdot}OH$ or $R{\cdot}C_6H_4{\cdot}CO_2H$. On the other hand, the theory of unitary catalytic action leads to an opposite conclusion in the case of catalysis by acids; for it presumes that the attack of the acid or kation would be of the indirect type and would operate on the most basic part of the molecule in proportion to its basicity; and thus the strengths of the bases, $R{\cdot}C_6H_4{\cdot}NH_2$, etc., should determine the velocities of isomerisation. The sequence thus indicated is the reverse of that corresponding to the duplex mechanism. Under constant conditions of acid catalysis, five tetra-acetylglucosidylarylamines (R = H, *p*-Cl, *p*-Br, *p*-Me, *p*-MeO) and five tetramethylglucosidylarylamines gave velocity coefficients agreeing with the sequence required by the unitary mechanism.[42] As regards basic catalysis, both mechanisms lead to the same inference, and the results are, therefore, equally consistent with both.

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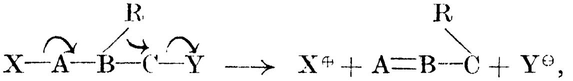
[38] *J.*, 1926, 1477; A., 1926, 939.

[39] *J.*, 1928, 1584; A., 870.

[40] *J.*, 1925, 127, 1371; *A.*, 1925, i, 886.

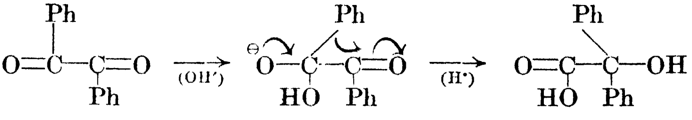
[41] *Loc. cit.*

(c) *Pinacolic systems.* A general expression, involving what is called the " pinacolic electron-displacement," and embracing the pinacol–pinacolin, Wagner–Meerwein and related transformations, has been given in the following form :



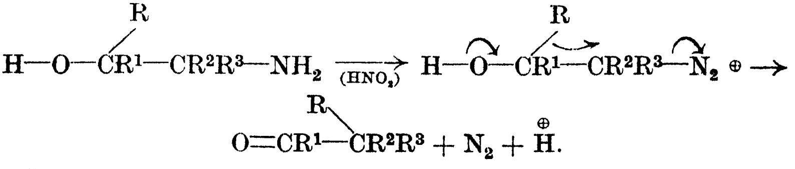
$$X{-}A{-}\overset{R}{B}{-}C{-}Y \longrightarrow X^{\oplus} + A{=}B{-}\overset{R}{C} + Y^{\ominus},$$

in which the tendency of X to part from, and of Y to retain, electrons during ionisation or combination with a reagent supplies the driving force of the mechanism.[43] In the changes mentioned, X is usually an ionisable hydrogen atom and Y a potential anion such as hydroxyl or halogen, but in certain cases a preliminary reaction is necessary to provide the complete system; for instance, in the benzil–benzilic acid change the effect of X is provided by a negative pole formed by the preliminary addition of a hydroxide ion :



$$O{=}\overset{Ph}{C}{-}\underset{Ph}{C}{=}O \xrightarrow[(OH')]{} {}^{\ominus}O{-}\underset{HO}{C}{-}\underset{Ph}{\overset{Ph}{C}}{=}O \xrightarrow[(H^{\cdot})]{} O{=}\underset{HO}{C}{-}\underset{Ph}{\overset{Ph}{C}}{-}OH$$

and in pinacolic deamination a positive pole, to take charge of the duties of Y, must first be created by the action of nitrous acid on the amino-group :



$$H{-}O{-}\overset{R}{C}R^1{-}CR^2R^3{-}NH_2 \xrightarrow[(HNO_2)]{} H{-}O{-}\overset{R}{C}R^1{-}CR^2R^3{-}N_2{}^{\oplus} \longrightarrow O{=}CR^1{-}\overset{R}{C}R^2R^3 + N_2 + \overset{\oplus}{H}.$$

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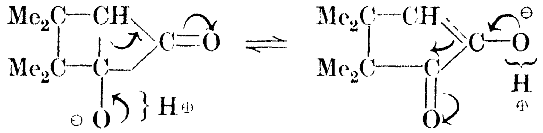
[42] J. W. Baker *loc. cit.*; *J.*, 1928, 1979; **A.**, 967.

[43] C. K. Ingold and C. W. Shoppee, *J.*, 1928, 365; **A.**, 414; C. W. Shoppee, *Proc. Leeds Phil. Soc.*, 1928, i, 301; **A.**, 1135.

During the year, two related, highly mobile, cyclic prototropic systems have been reported in which the reversible changes are considered to depend on this mechanism. Analogous, but much less mobile, open-chain systems, in which a change in only one direction has been observed, have also been described.

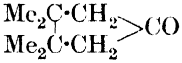
In the first of the cyclic systems R is carbon, so the displaced electrons form part of its octet. The parent compound of the group concerned is the hydroxy-ring-ketone for which F. Francis and F. G. Willson originally adduced formula (XIV).[44] It is now shown that the same compound is also to be represented by formula (XV),[45] for both typical hydroxyl and typical carbonyl reactivity is exhibited in positions which can be shown to be identically oriented in the 5-carbon nucleus; further, reduction yields two crystalline ketones, identified as (XVI) and (XVII), and reduction of the oximes or their acyl derivatives gives the two corresponding crystalline amines, (XVIII) and (XIX):

(XIV.)

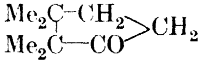


(XV.)

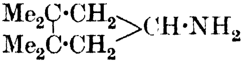
(XVI.)



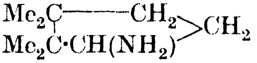
(XVII.)



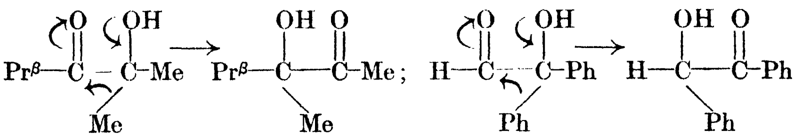
(XVIII.)



(XIX.)



The irreversible changes, which may be presumed to be of the same type, are the conversion of *iso*butyryldimethylcarbinol into acetylmethyl*iso*propylcarbinol,[46] and of diphenylglycollaldehyde into benzoin:[47]



Since the conditions in which these changes occur involve heating with alcoholic sulphuric acid to a comparatively high temperature (*e.g.*, 120°), it appears that the mobility of these open-chain pinacolic systems is smaller than that of the cyclic system.

In the second cyclic system, R (see general formula, p. 124) is hydrogen, which with its shared duplet is assumed to be transferred to an adjacent carbon atom. The compound, represented by the formulæ (XX, XXI), is crystalline and the evidence for the double

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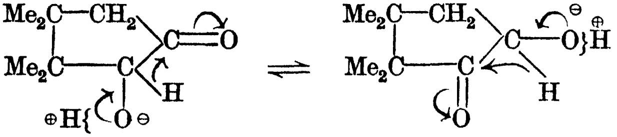
[44] *J.*, 1913, **103**, 2238.

[45] C. K. Ingold and C. W. Shoppee, *loc. cit.*

[46] (Mlle.) A. I. Oumnov, *Bull. Soc. chim.*, 1928, [iv], **43**, 568; **A.**, 740.

[47] S. Danilov, *Ber.*, 1927, **60**, [*B*], 2390; **A.**, 1928, 64.

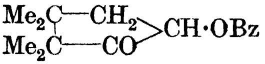
(XX.)

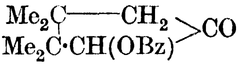


(XXI.)

formulation[48] is that it is benzoylated and oximated both in the symmetrical and in the unsymmetrical positions with respect to the two *gem*-dimethyl groups, giving a separable mixture of benzoyl derivatives which are proved by reduction of their oximes to have constitutions (XXII) and (XXIII), and a non-separable mixture of oximes reducible to the amines (XVIII) and (XIX). Thus the evidence of dual constitution is as complete as in the former cyclic case, but the evidence of mechanism is complicated here by the possibility of a sequence of triad changes involving the intermediate (XXIV). This alternative is, however, rendered improbable by the following consideration: the interconversion of (XX) and (XXI) is obviously rapid and reversible; therefore, if it occurs by way of

(XXII.)

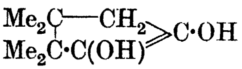


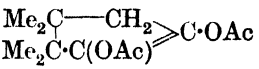


(XXIII.)

(XXIV), this must be formed, not necessarily in high concentration, but at any rate *rapidly*, and from *both* ketonic isomerides; therefore, if the compound is treated with excess of an acylating agent, (XXIV) should be formed, and should give (XXV) on acylation; actually, however, no such compound could be obtained, and the acylation could not be carried beyond the stage at which one acyl group had been introduced, as in the formation of (XXII) and (XXIII).

(XXIV.)





(XXV.)

Without some such evidence indicating the exclusion of a triad mechanism, instances of this change naturally lose something of their significance; nevertheless, it is interesting to notice that every one of the eight examples which have been studied by A. Favorski[49] and his pupils and relate to open-chain pinacolic systems shows the same reduced mobility which characterises the corresponding reaction involving alkyl-transference in open-chain systems. This may be regarded as indirect evidence in favour of a pinacolic mechanism. The following transformation is typical:

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[48] C. W. Shoppee, *J.*, 1928, 1662 (not abstracted).

[49] *Bull. Soc. chim.*, 1926, [iv], **39**, 216; 1928, [iv], **43**, 563, 573; **A.**, 1926, 500; 1928, 739, 752.

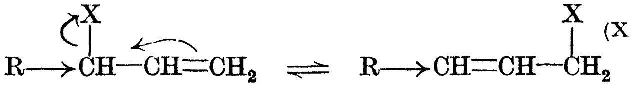
$$C_6H_5{\cdot}CO{\cdot}CH(OH){\cdot}CH_3 \xrightarrow[\text{alcohol at 120—125°}]{H_2SO_4\text{ in}} C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}CH_3$$

and all of them depend on experimental conditions similar to that indicated beside the arrow.

(II) *Anionotropy.*—Last year's account of this subject dealt with simple and developed dyad systems, that is, with the ordinary nitrogen and sulphur ψ-bases. Continuing the matter, simple and developed triad systems will now be discussed, together with some special applications.

(a) *The three-carbon system.* The first noteworthy theoretical contribution is that of A. Gillet,[50] who, in 1922, directed attention to the existence of known cases of the $\alpha\gamma$-migration of "negative radicals," and even went so far as to suggest that the 1 : 4-addition of halogens to conjugated systems consisted of 1 : 2-addition followed by 2 : 4-migration of halogen; but at that time, it was, of course, difficult fruitfully to discuss the electrochemical nature of the phenomenon under consideration. C. Prévost [51] raised the matter again in 1927. His basis was the theory of alternate polarities and Lowry's semi-polar ethylenic linking, but these conceptions did not enable him further to advance the problem of elucidating the conditions under which anionotropy is manifested. This year the view has been put forward [52] that, whereas the mobile group separates as its anion under the joint influence of external attraction by kations or polar molecules and internal electron-release by neighbouring groups, prior to re-association of the ions, the kationic charge undergoes distribution by tautomeric electron-displacement in a manner determined by the electron-affinities of the various groups attached to the system. From this it follows that the facility with which X separates as an anion from the system

(XXVI.)



$$R\longrightarrow\overset{X}{\overset{|}{C}}H-CH=CH_2 \rightleftharpoons R\longrightarrow CH=CH-\overset{X}{\overset{|}{C}}H_2$$

(XXVII.)

will depend *inter alia* (1) on the intrinsic anionic stability of $X^{\ominus}$, as indicated, for example, by the strength of the acid HX, (2) on the presence of external kations, or, in their absence, on the polar field of the neutral solvent, as indicated by its dielectric constant, (3) on the capacity of R to supply electrons to the depleted carbon atom, as shown by its *op*-orienting power in aromatic substitution. The evidence [53] relating to these points may now be considered.

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[50] *Bull. Soc. chim. Belg.*, 1922, **31**, 366; *A.*, 1923, ii, 147; see also *Bull. Soc. chim.*, 1927, [iv], **41**, 927; **A.**, 1927, 921.

[51] *Compt. rend.*, 1927, **185**, 132; **A.**, 1927, 851.

[52] H. Burton and C. K. Ingold, *J.*, 1928, 904; **A.**, 634; H. Burton, *ibid.*, p. 1650; **A.**, 881.

First, when R = Ph and X = OH, the mobility is small, because α-phenylallyl and cinnamyl alcohols are obtainable separately, and each can be esterified without a change of structure. On the other hand, the corresponding esters (X = $\cdot O\cdot CO\cdot CH_3$, $\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$-*p*) undergo smooth interconversion in the direction (XXVI) ⟶ (XXVII), in solvents of which chlorobenzene, acetic anhydride, and benzonitrile are examples. Finally, the corresponding bromohydrocarbons (X = Br) are so mobile that only one of them (XXVII) can be isolated. This relationship, namely, that, when R remains the same, the mobility changes with the nature of X in the direction Halogens>·OAcyl>·OH, is also true for all the anionotropic systems referred to in other connexions below. The order obviously corresponds with the anionic stabilities of the groups as indicated by the relative strengths, as acids, of strong acids, weak acids, and water. That the group eliminated actually does leave the system as an anion has been proved by allowing the change (R = Ph, X = $O\cdot CO\cdot C_6H_4\cdot NO_2$-*p*) to proceed in the presence of a salt (tetramethylammonium acetate) the anions of which compete with the X-anions returning to the system, so that a mixture is produced.

Secondly, the effect of the polar field of the solvent is shown by the fact that in the same example the rate of conversion at constant temperature varies in the order benzonitrile, acetic anhydride > chlorobenzene>*p*-xylene. In the first two the change is complete and rapid, in the third, complete but considerably slower, and in the fourth, very slow and only partial. The corresponding dielectric constants are approximately 26, 21, 6, 2.

Finally, an examination of a number of three-carbon anionotropic systems terminated at one end or at both ends by various groups shows that the order of facilitation is $p\text{-}Cl\cdot C_6H_4 \gg p\text{-}Me\cdot C_6H_4 > C_6H_5 \gg Me > H$, the last inequality being already clear from J. Baudrenghien's work.[54] This order agrees, as it theoretically should, with the *op*-orienting sequence Cl>Me>H, as inferred in the ordinary way from the proportions of isomerides formed in benzene substitutions.

In all these systems the position of equilibrium appears to follow the simple rule that the potential anion will preferentially occupy the position adjacent to the least activating of the terminal groups.

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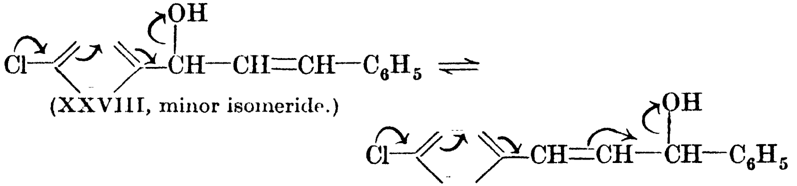
[53] *Loc. cit.*

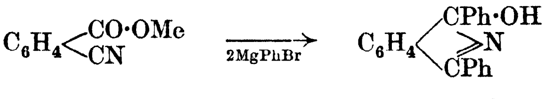
[54] *Bull. Soc. chim. Belg.*, 1922, **31**, 160; 1923, **32**, 337; *A.*, 1922, i, 710; 1924, i, 133. See also R. Locquin and S. Wouseng, *Compt. rend.*, 1922, **174**, 1711; *A.*, 1922, i, 710; M. Bouis, *ibid.*, 1926, **182**, 788; **183**, 133; **A.**, 1926, 495, 935; C. Prévost, *Ann. Chim.*, 1928, [x], **10**, 147; **A.**, 1211.

As regards the two major inequalities in the above sequence, the following may be said : (*a*) The relation, aryl$\gg$alphyl, which applies also to the facilitation of prototropy, was attributed on p. 121 to the capacity of the aromatic nucleus for tautomeric displacements in either direction according to the requirements of the side-chain reaction. (*b*) The strong facilitation by *p*-chlorophenyl (which should be enhanced in *p*-methoxyphenyl, compare p. 122) arises from the possibility (dependent on the presence in chlorine of unshared valency electrons) of tautomeric electron-displacements *in the direction required* for the liberation of the anion and the absorption of the charge; the effect of the presence of this machinery, ever ready to assist the attack of a reagent (*e.g.*, solvent) molecule, far outweighs the opposing permanent inductive effect of the halogen. The result is that even the alcohols (XXVIII) and (XXIX) (still more their acetates or bromides) cannot separately be isolated but immediately yield their equilibrium mixture :


(XXVIII, minor isomeride.)

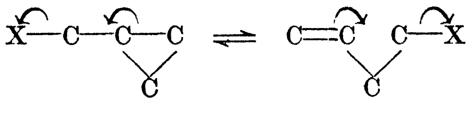
(XXIX, major isomeride.)

Little is known at present with regard to triad anionotropy in nitrogenous systems, but an important parent substance, derivatives of which may exhibit the phenomenon, has been prepared by D. R. Boyd and D. E. Ladhams by a simple method apparently capable of wide exploitation. The substance referred to is 1-hydroxy-1 : 3-diphenyl*iso*indole, which is obtained from *o*-cyanobenzoic ester by the Grignard reaction :[55]



$$C_6H_4{<}{}^{CO\cdot OMe}_{CN} \xrightarrow[2MgPhBr]{} C_6H_4{<}{}^{CPh\cdot OH}_{CPh}{>}N$$

(b) *Cyclic systems.* P. Bruylants and A. Dewael[56] have made an extremely interesting discovery, which proves the possibility of three-carbon ring-chain anionotropy of the following type (intermediate kations omitted from formulæ) :



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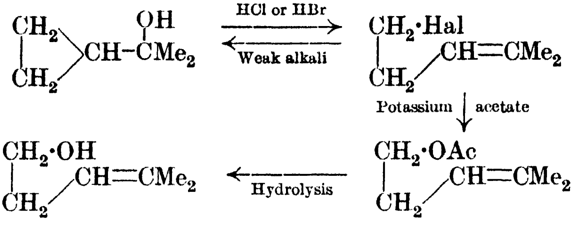
[55] *J.*, 1928, 2089; **A.**, 1140.

[56] *Bull. Acad. roy. Belg.*, 1928, [v], **14**, 140; **A.**, 518.

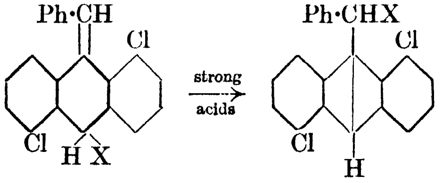
The transformations which have been realised are indicated in the scheme given below :



No direct interconversion of *isomerides* was encountered in this work, but now that it is understood (p. 128) that the production of an isomeride by anionotropic change depends on the absence from the medium of foreign anions which would compete with the eliminated anion in returning to the system, it should readily be possible to effect an analogous isomeric change by allowing suitable esters of either alcohol to rearrange in an organic solvent of sufficiently high dielectric constant.

Another interesting set of examples has been discovered in the anthracene series by E. de B. Barnett, M. A. Matthews, and J. W. Cook,[57] and its nature recognised by the last-named author. The transformations are of the following type and are catalysed by acids (X = OH, OMe, OAc, etc.) :

(XXX.)



(XXXI.)

The 5-chlorine atom and the lateral aromatic rings are obviously concerned in determining the lability of X in (XXX), and the replacement of the *meso*-hydrogen atom by a phenyl group increases the relative stability of form (XXXI). An interesting observation was made in the case for which X = OH, namely, that whilst the above anionotropic change was brought about by strong acids, an analogous prototropic change to the anthranol (anthrone) was effected by strong alkalis; thus, in either case, the sign of the catalytic ion is the opposite of that of the mobile ion of the system activated by the catalyst—a clear indication of the mechanism of homogeneous catalysis in isomeric change generally :

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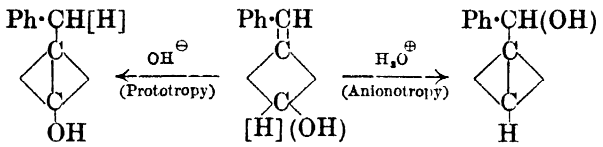
[57] *Ber.*, 1927, **60**, [*B*], 2353; **A.**, 1928, 52; J. W. Cook; *ibid.*, p. 2366; **A.**, 1928, 53; *J.*, 1928, 2798; **A.**, 1366.



(c) *Application to additions to conjugated systems.* The elucidation of some of the principal conditions governing the manifestation of anionotropy has led to the proposal of a theory of orientation in additions to conjugated systems.[58] Addenda are classified according as they introduce potential anions (*e.g.*, Hal) or kations (*e.g.*, H) into the system, and the cases involving the introduction of potential anions into systems containing electron-releasing substituents are developed in some detail as an illustration of the manner in which the theory can be handled.

The possibility of the occurrence, by Gillet's mechanism, of apparent 1 : 4- or 1 : 6-addition has now been proved for the 1 : 4-dibromide of butadiene,[59] the 1 : 6-dibromide of hexatriene,[60] and the 1 : 4-hydrobromides of *iso*prene [61] and $\beta\gamma$-dimethylbutadiene,[62] but it has been found that the rate of isomerisation of an isolated 1 : 2-dibromide is too slow to account for more than a part of the 1 : 4-compound formed during addition ; [63] so that, obviously, Gillet's mechanism is partly, but not wholly, correct.

The new suggestion depends, so far as halogen additions are concerned, on a view with regard to their additions to simple ethylenic linkings, which is reached by combining Soper and Smith's proof that in halogen-substitutions the attack is by the molecule and not by either of its ions even in an ionising solvent,[64] with A. W. Francis' demonstration [65] that in halogen additions one ion enters before the other. Francis thought that a pre-formed ion first attacked the unsaturated linking, but the conclusion now advanced, namely, that the second ion is liberated only during the addition of the first, is expressed in the following illustration, which incidentally explains how halogens in aqueous solution lead to the formation of halogenohydrins—a reaction often erroneously attributed to the addition of hypohalous acid, despite that this usually reacts far too slowly to be the cause :

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[58] H. Burton and C. K. Ingold, *loc. cit.*

[59] C. Prévost, *Compt. rend.*, 1926, **183**, 1292 ; **A.**, 1927, 131 ; E. H. Farmer, C. D. Lawrence, and J. F. Thorpe, *J.*, 1928, 729 ; **A.**, 504.

[60] C. Prévost, *Compt. rend.*, 1927, **184**, 485 ; **A.**, 1927, 337 ; E. H. Farmer, B. D. Laroia, T. M. Switz, and J. F. Thorpe, *J.*, 1927, 2937 ; **A.**, 1928, 151.

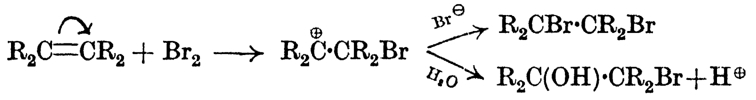
[61] L. Claisen, *J. pr. Chem.*, 1922, **105**, 68 ; *A.*, 1923, i, 1050.

[62] A. G. Bergmann, *J. Russ. Phys. Chem. Soc.*, 1920, **52**, 37 ; *A.*, 1922, i, 1106.

[63] E. H. Farmer, C. D. Lawrence, and J. F. Thorpe, *loc. cit.*

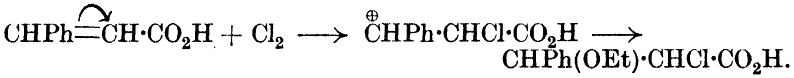
[64] *Ann. Reports*, 1926, **23**, 135.

[65] *J. Amer. Chem. Soc.*, 1925, **47**, 2340 ; *A.*, 1925, i, 1261.



$$R_2C\overset{\curvearrowright}{=}CR_2 + Br_2 \longrightarrow R_2\overset{\oplus}{C}\cdot CR_2Br \begin{array}{l} \xrightarrow{Br^{\ominus}} R_2CBr\cdot CR_2Br \\ \xrightarrow{H_2O} R_2C(OH)\cdot CR_2Br + H^{\oplus} \end{array}$$

Confirmation is forthcoming, for instance, from the work of E. L. Jackson and L. Pasiut,[66] who have shown *inter alia* that ethyl-alcoholic chlorine converts cinnamic acid into α-chloro-β-ethoxy-β-phenylpropionic acid :



$$CHPh\overset{\curvearrowright}{=}CH\cdot CO_2H + Cl_2 \longrightarrow \overset{\oplus}{C}HPh\cdot CHCl\cdot CO_2H \longrightarrow CHPh(OEt)\cdot CHCl\cdot CO_2H.$$

The authors attribute the reaction to the addition of ethyl hypochlorite, but if this were so the product should surely be β-chloro-α-ethoxyphenylpropionic acid, and the same applies to the products of the addition of halogens in water to cinnamic acid[67] and amylene.[68]

Pursuing the same illustration, namely, the addition of bromine, it is deduced that, since the second bromine atom is liberated (as anion) only during the addition of the first, the initial product of addition to a butadienoid system may correctly be described as consisting of the ions of the 1 : 2-dibromide. If the conditions are not favourable to ionic *dissociation*, the ions will associate (co-ordinate) to give the 1 : 2-dibromide; on the other hand, if the solvent and the temperature are conducive to dissociation, it will occur, and then the anionotropic system will attain equilibrium by distribution of the kationic charge; and, in a general case, a mixture of bromides will result, the composition of which will depend on the attached groups in the manner indicated in section (IIa). Furthermore, the rate of the change (A) ⟶ (C) will not necessarily bear any simple relation to the rate of the change (B) ⟶ (C) :

$$\begin{tikzcd}
\text{(A) Reagents} \arrow[r] & \text{Ions of 1 : 2-Bromide} \arrow[r, leftrightarrows] \arrow[d, leftrightarrows] & \text{1: 2 -Bromide (B)} \\
 & \text{Ions of 1 : 4-Bromide} \arrow[r, leftrightarrows] & \text{1 : 4-Bromide (C)}
\end{tikzcd}$$

This view appears consistent with the available data, and is used, for example, to explain the much-discussed 1 : 2-addition of bromine to αδ-diphenylbutadiene, and the 3 : 4-addition of the same halogen to α-phenylbutadiene, on the grounds of the much stronger facilitation of anionotropic change by α-aryl than by α-alphyl (p. 129).

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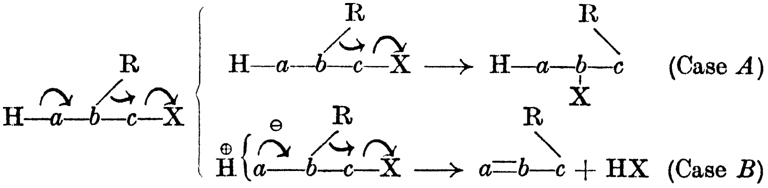
[66] *J. Amer. Chem. Soc.*, 1927, **48**, 2071; **A.**, 1927, 969.

[67] J. Read and A. C. P. Andrews, *J.*, 1921, **119**, 1774.

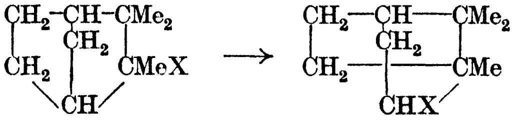
[68] J. Read and W. G. Reid, *J.*, 1928, 1487; **A.**, 866.

Thus, in the former example, if Ph·CHBr·$\overbrace{\text{CHBr·CH:CH}}$·Ph, or its ions, were first formed (the bracket indicates the tautomeric system), the relatively slow and incomplete change (promoted by Ph·CHBr·, *i.e.*, alphyl) to Ph·$\underbrace{\text{CHBr·}\overbrace{\text{CH:CH}}}\overbrace{\text{·CHBr}}$·Ph would be at once succeeded by the much more rapid and complete change (promoted by Ph, *i.e.*, aryl) to Ph·CH:CH·CHBr·CHBr·Ph. Thus the 1 : 4-bromide is not isolated, and the main product is the 1 : 2(= 3 : 4)-dibromide.

(d) *Application to the Wagner and the pinacol–pinacolin rearrangements.* This application was not dealt with in Burton and Ingold's paper, but may be considered here in relation to observations which have been made since this subject was last discussed in these Reports. As the general formula for pinacolic electron-displacement shows (below), two important factors determining the direction and facility of the reaction are the tendencies of H and X to separate as kation and anion respectively. Two cases which are specially simple in relation to the theory of anionotropy are those which arise (*A*) when the ionisation of H is attended with such difficulty that the ionisation of X dispenses with its aid and acts alone, (*B*) when the ionisation of H is so facile that again the determining condition is the ionisation of X (the ionisation of H alone will not determine migration because it does not disrupt an octet) :



Case (*A*) is immediately recognisable by the fact that no elimination occurs; it arises in certain cases in which the atom *a* is a carbon atom, for instance, in the conversion of camphene hydrate esters into *iso*bornyl esters :



The deduction here is that the facility of the change in such a series of examples should depend, first, on the anionic stability of the potential anion, secondly, on the dielectric constant of the (neutral) solvent. Actually it has been found [69] that the facility of the change decreases with varying X in the order sulphonate$>$bromide$>$chloride$>$trichloroacetate$>$*m*-nitrobenzoate, which is the order of decreasing strengths of the acids HX; and that it decreases with varying neutral solvents in the order nitrobenzene$>$benzonitrile$>$chlorobenzene$>$benzene$>$ligroin, which is the order of decreasing dielectric constant (36, 26, 6, 2·3, 1·9, respectively). Certain acidic and ψ-acidic solvents give rise to velocities higher even than that observed with nitrobenzene (compare p. 127).

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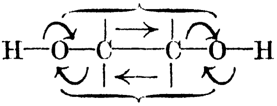
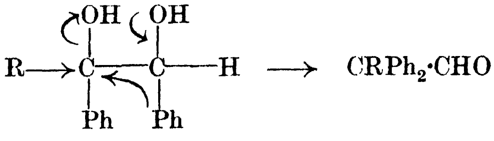
[69] H. Meerwein, *Annalen*, 1927, **453**, 16; **A.**, 1927, 568.

Case (*B*) arises where *a* is an oxygen atom. This is so in the pinacol–pinacolin change, in which also X is a hydroxyl group, so that group-migration might obviously proceed in either of two directions :



It may be deduced that the actual direction will be determined, not by the anionic stabilities of the two potential anions, for they are the same, nor by the polar constants of the medium, for it will affect both ionisations nearly equally, but by the third factor concerned in anionotropy, namely, the capacity for electron-release of the attached groups (provided that identical or comparable migrating groups are concerned).[70] The relationship (pp. 128, 129) is H$<$alphyl$<$aryl without *op*-unshared electrons$<$aryl with *op*-unshared electrons, and French chemical literature contains a mass of data from which it may be exemplified. For instance, the first inequality (H$<$alphyl) may be illustrated by the following changes (R = Me or Et) : [71]



The second (alphyl$<$aryl) is shown, for example, by the following transformations (Ar = Ph or anisyl) [72] :

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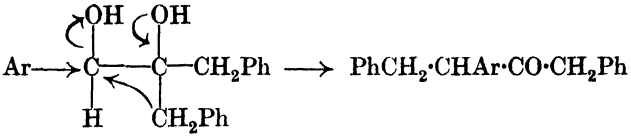
[70] This depends mainly on their relative abilities to hold their shared electrons, and this may be either inferred theoretically on principles similar to those employed in considering the facilitation of prototropy, or deduced from independent observations in other fields of organic chemistry, as, for instance, the facility of elimination of groups as saturated hydrocarbons from quaternary phosphonium hydroxides, or from sulphinates in the presence of alkali.

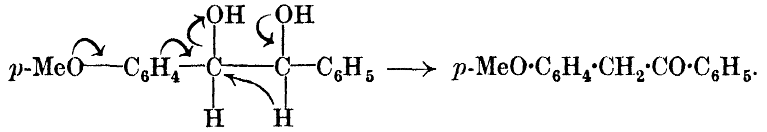
[71] A. Orékhov and M. Tiffeneau, *Compt. rend.*, 1926, **182**, 67; **A.**, 1926, 171.

[72] M. Tiffeneau and J. Levy, *ibid.*, 1926, **183**, 1112; **A.**, 1927, 154.



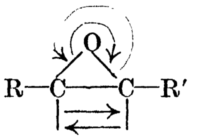
$\longrightarrow PhCH_2{\cdot}CHAr{\cdot}CO{\cdot}CH_2Ph$

The third inequality (aryl without unshared *op*-electrons < aryl with such) may be illustrated by reference to the change undergone by phenyl-*p*-anisylglycol : [73]

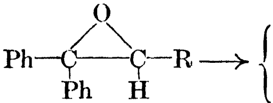


$\longrightarrow p\text{-}MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5.$

Similar considerations apply to the rearrangement of ethylene oxides, which may yield either of two ketones according to the relative capacities for electron-release of the groups R and R′ (XXXII). Illustrating from a series of ethylene oxides which has recently been investigated,[74] namely, those of the general formula (XXXIII), the migration proceeds from right to left (despite the great migratory tendency of phenyl) when R is Me, Et, Pr$^\alpha$, Pr$^\beta$, Bu$^\alpha$, Bu$^\beta$, or benzyl, and the ketone (XXXIV) is a major product (aryl>alphyl). The same is true when R = Ph (Ph_2>Ph), but when R is *p*-anisyl the direction of migration is reversed and the product is the ketone (XXXV) (*p*-anisyl>phenyl) :



(XXXII.)



(XXXIII.)

$Ph_2CH{\cdot}CO{\cdot}R$ (XXXIV.)

$Ph{\cdot}CO{\cdot}CHPhR$ (XXXV.)

(III) *Valency Tautomerism.*—This title is used to connote electromerism, not in an ion, but within a neutral molecule.

(a) *Ring-chain system.* The suggestion, foreshadowed in 1913 by F. Francis and F. G. Willson,[75] that certain substitution products of phorone represent balanced examples of ring-chain valency tautomerism, has been emphasised during the year.[76] Phorone itself is undoubtedly mainly of type (XXXVI) : it is a bright yellow substance, possessing a high refractivity (exaltation 3 units) and a nearly normal parachor; it is also strongly unsaturated, reacting readily with halogens and hydrogen halides and giving di*iso*butyl ketone (XXXIX) on reduction. A marked approach towards the saturated condition is, however, observed in dibromophorone, which may be represented by (XXXVII): it is only feebly coloured, its exaltation of refractivity is much smaller (1·4 units), and its parachor abnormally low (anomaly, —10·8 units); it is unaffected by bromine, rather difficult to oxidise, and on reduction gives *both* open-chain and cyclic products. Bromohydroxyphorone (XXXVIII), on the other hand, is undoubtedly a cyclic substance and yields the ketone (XL) on reduction; it is colourless, and the refractivity (negative anomaly) and parachor (anomalies —17 to —27 units) of its ethers and esters confirm the conclusion.

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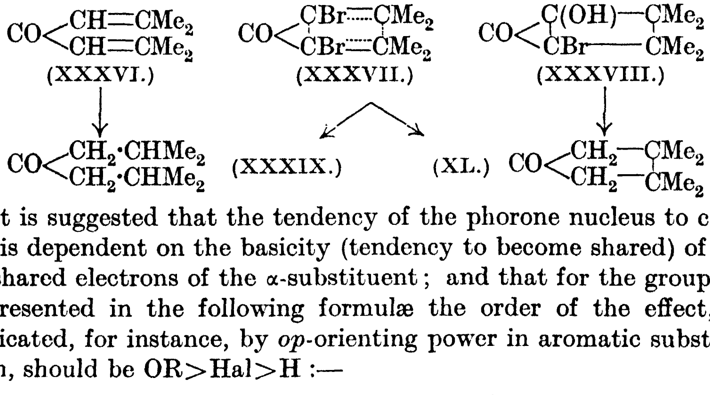
[73] A. Orékhov and M. Tiffeneau, *Bull. Soc. chim.*, 1925, [iv], **37**, 1410; **A.**, 1926, 172.

[74] R. Legrave, *Ann. Chim.*, 1927, [x], **8**, 363; **A.**, 1928, 270.

[75] *Loc. cit.*

[76] C. K. Ingold and C. W. Shoppee, *loc. cit.*; *J.*, 1928, 1868; **A.**, 1014; S. Sugden, *J.*, 1928, 410; **A.**, 416.



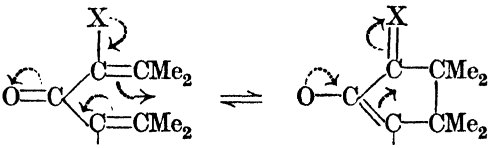
$$\mathrm{CO}\left<\begin{matrix}\mathrm{CH{=}CMe_2}\\ \mathrm{CH{=}CMe_2}\end{matrix}\right. \qquad \mathrm{CO}\left<\begin{matrix}\mathrm{CBr{=}CMe_2}\\ \mathrm{CBr{=}CMe_2}\end{matrix}\right. \qquad \mathrm{CO}\left<\begin{matrix}\mathrm{C(OH){-}CMe_2}\\ \mathrm{CBr{-}CMe_2}\end{matrix}\right.$$

(XXXVI.) (XXXVII.) (XXXVIII.)

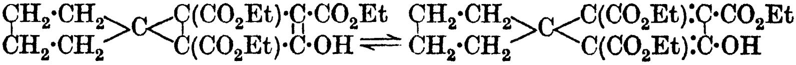
$$\mathrm{CO}\left<\begin{matrix}\mathrm{CH_2{\cdot}CHMe_2}\\ \mathrm{CH_2{\cdot}CHMe_2}\end{matrix}\right. \qquad \mathrm{CO}\left<\begin{matrix}\mathrm{CH_2{-}CMe_2}\\ \mathrm{CH_2{-}CMe_2}\end{matrix}\right.$$

(XXXIX.) (XL.)

It is suggested that the tendency of the phorone nucleus to close up is dependent on the basicity (tendency to become shared) of the unshared electrons of the α-substituent; and that for the groups X represented in the following formulæ the order of the effect, as indicated, for instance, by *op*-orienting power in aromatic substitution, should be OR>Hal>H :—



(b) *Intra-annular systems.* The reactions and degradation of the system



$$\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!>\!\mathrm{C}\!\left<\begin{matrix}\mathrm{C(CO_2Et){\cdot}C{\cdot}CO_2Et}\\ \mathrm{C(CO_2Et){\cdot}C{\cdot}OH}\end{matrix}\right. \rightleftharpoons \begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!>\!\mathrm{C}\!\left<\begin{matrix}\mathrm{C(CO_2Et){:}C{\cdot}CO_2Et}\\ \mathrm{C(CO_2Et){:}C{\cdot}OH}\end{matrix}\right.$$

have now been investigated with the result that the importance of the bridged-phase appears to be greater than amongst the corresponding *cyclo*hexane*spiro*-compounds, but smaller than for the analogues of the *gem*-dimethyl series.[77] This result is in keeping with the order of the effects of the *gem*-dimethyl, *cyclo*pentane, and *cyclo*hexane groups in the other chemical and physical phenomena in which their relative influence has been traced.

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[77] F. R. Goss, *J.*, 1928, 1306; **A.**, 758.

Aromatic Substitution and Side-chain Reactivity.

(Continued from *Ann. Reports*, 1926, **23**, 129; 1927, **24**, 148.)

This year's work has been characterised by further developments regarding the genesis and transmission of orienting effects, and by a signal advance in the direction of connecting theories of orientation with the quantitative conceptions relating to reaction dynamics.

(I) *Genesis of Orienting Effects.*—(a) *Positive poles.* It was previously shown that the *m*-orienting effect produced by a given positive pole decreases regularly with the lengthening of the carbon chain interposed between the pole and the benzene nucleus. By examination of the nuclear substitution of a series of substances with comparable poles, similarly situated with regard to the nucleus, it has now been shown that *m*-orientation decreases regularly with the atomic number of the charged atom.[78] These two effects may be illustrated together by the following table, in which the figures denote the proportions of *m*-isomeride formed on nitration of the kations represented. D. Vorländer and E. Siebert's result for phenyltrimethylammonium is included, and, except where indicated to the contrary, the other nitrations were carried out at or below 0° :

$\overset{+}{N}Me_3$ 100%*†	$CH_2{\cdot}\overset{+}{N}Me_3$ 88%	$CH_2{\cdot}CH_2{\cdot}\overset{+}{N}Me_3$ 19%	$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}Me_3$ 5%
$\overset{+}{P}Me_3$ 100%†‡	$CH_2{\cdot}\overset{+}{P}Me_3$ 10%	—	—
$\overset{+}{As}Me_3$ 98%†	$CH_2{\cdot}\overset{+}{As}Me_3$ 3·4%		
$\overset{+}{Sb}Me_3$ 86%‡	—		

* *Ber.*, 1919, **52**, 283; *A.*, 1919, i, 319.
† Temperature 60° or above.
‡ Sulphuric acid added.

From these data it appears, not only that the attraction of the aromatic electrons by the positive pole is decreased with relay through intervening carbon atoms, but also that the portion of the positive electrical field, which, emanating from the central nucleus of the charged atom, reaches beyond the surface of the atom and thus becomes available for the creation of orienting effects, is smaller the larger the atom. Thus the octets of the intercalated carbon atoms and the outer electron groups of the larger charged atoms constitute two different types of electron-screen through which the positive field may become damped during its passage to the aromatic nucleus.

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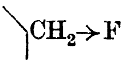
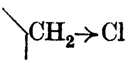
[78] C. K. Ingold, (Miss) F. R. Shaw, and I. S. Wilson, *J.*, 1928, 1280; **A.**, 782. Reference to F. Challenger, *loc. cit.*

The experiments referred to may also be used to illustrate the general principle that the stronger the *m*-orientation the slower should be the substitution.[79] Failure to recognise this has led to the claiming of an anomaly in the nitration of benzylaniline sulphate.[80] This base is a comparatively strong one, and should exist wholly as salt in the concentrated sulphuric acid used as solvent. Substitution should therefore occur in the ring *less* strongly affected by the pole (the *benzyl* ring); and, to judge from the case of dibenzylamine,[81] the product should consist of about 75% of the *m*-nitro-derivative, the remainder being principally the *p*-isomeride. Actually 65% of *m*-nitrobenzylaniline and 10% of the *p*-nitrobenzyl isomeride were isolated, and 25% of a mixture containing both remained unseparated. Thus the case creates no theoretical difficulty, but merely constitutes another illustration of the utility of envisaging the substitution of polynuclear systems in the manner explained in the Report for 1926.

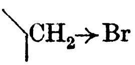
(b) *Halogens.* Benzyl fluoride has been prepared for the first time and its nitration studied.[82] The nitration of benzyl chloride has been revised, and that of benzyl bromide studied for the first time.[83] The figures below, which refer to the proportion of *m*-substitution in acetic anhydride at about 25°, show that the electron-affinity of these neutral halogen substituents decreases with increasing size, just as with the positively charged elements considered above; the result may again be ascribed to the weaker positive field at the surface of the larger atom :


$CH_2 \rightarrow F$

17·5%


$CH_2 \rightarrow Cl$

12·0%


$CH_2 \rightarrow Br$

6·9%

(c) *Triple linkings.* Phenylpropiolic acid yields 8% of the *m*-nitro-derivative on nitration in absolute nitric acid at —30°. The ethyl ester behaves similarly, and the contrast between these results and the exclusive *op*-nitration of cinnamic acid and its esters has been discussed in the light of a hypothesis which brings to a common focus a number of facts relating to the chemistry of triply linked systems.[84]

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[79] C. K. Ingold and (Miss) F. R. Shaw, *J.*, 1927, 2918; **A.**, 1928, 164.

[80] J. Reilly, J. J. Moore, and P. J. Drumm, *J.*, 1928, 563; **A.**, 514.

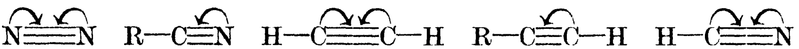
[81] F. R. Goss, C. K. Ingold, and I. S. Wilson, *J.*, 1926, 2440; **A.**, 1926, 1132.

[82] C. K. Ingold and (Mrs.) E. H. Ingold, *J.*, 1928, 2249; **A.**, 1126.

[83] B. Flürscheim and E. L. Holmes, *ibid.*, p. 1607; **A.**, 876.

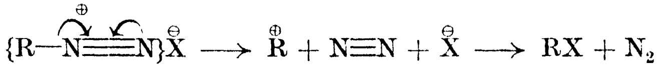
[84] J. W. Baker, K. E. Cooper, and C. K. Ingold, *ibid.*, p. 122; **A.**, 403.

The basic assumption (which it is not yet possible to *explain*, any more than the stability of the octet or the duplet can at present be explained) is that when six valency electrons are mutually shared by two atomic nuclei the system tends to appropriate additional electrons in order to form a stable association of eight, or, if possible, of ten electrons. The appropriation may, of course, be complete or incomplete, and it may affect two or four, shared or unshared, electrons.[85] The appropriation of unshared electrons leads to a loss of basic character, whereas the appropriation of shared electrons confers on the molecule a tendency to ionise. Thus the non-basic character of elementary nitrogen and of nitriles may be correlated with the acidity of acetylene [86] and hydrocyanic acid exactly as the feebly basic character of indole was correlated with the acidity of indene (p. 119) :



$$N\equiv N \qquad R-C\equiv N \qquad H-C\equiv C-H \qquad R-C\equiv C-H \qquad H-C\equiv N$$

Other points which are similarly explained are the instability of diazonium salts (*i.e.*, the greater tendency to the reaction

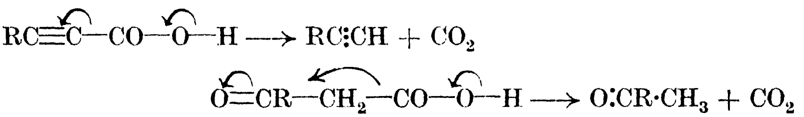


$$\{R-\overset{\oplus}{N}\equiv N\}\overset{\ominus}{X} \longrightarrow \overset{\oplus}{R} + N\equiv N + \overset{\ominus}{X} \longrightarrow RX + N_2$$

than towards the reaction

$$\{R-\overset{\oplus}{N}Alk_3\}\overset{\ominus}{X} \longrightarrow \overset{\oplus}{R} + NAlk_3 + \overset{\ominus}{X} \longrightarrow RX + NAlk_3$$

for corresponding R and X), the thermal instability of acetylenic acids, which resembles that of β-ketonic acids : [87]



$$RC\equiv C-CO-O-H \longrightarrow RC{:}CH + CO_2$$

$$O=CR-CH_2-CO-O-H \longrightarrow O{:}CR{\cdot}CH_3 + CO_2$$

and the fact that acetylenic acids are always much stronger (50—200 times) than the corresponding saturated or olefinic acids. In phenylpropiolic acid part of the electron-affinity of the triple linking is occupied in assisting the ionisation of the carboxyl group, and the rest exerts an attraction on the aromatic electrons which leads to *m*-orientation. Part of the large *m*-orienting action of the cyano-group [88] is attributed [84] to a similar cause.

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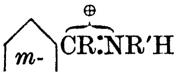
[85] The conception was foreshadowed by I. Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 903; *A.*, 1919, ii, 328) in that his nitrogen model corresponds to the special case of the complete appropriation of four unshared electrons; it also includes certain additional suppositions with regard to the presence and configuration of a binuclear octet with two more deeply imbedded electrons.

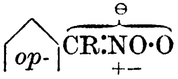
[86] R. Müller and H. Kumpfmiller have shown (*Z. Elektrochem.*, 1928, **34**, 70; **A.**, 481) that acetylene in acetone yields (solvated) hydrogen and carbon ions, $C_2H_2 \rightleftharpoons H^{\cdot} + C_2H' \rightleftharpoons 2H^{\cdot} + C_2''$, and that the latter attain equilibrium with neutral carbon at a carbon electrode.

[87] The formulæ are schematic only : probably the reactions are cyclic in character.

(d) *ψ-Bases and ψ-acids.* J. W. Baker has pointed out [89] that when a ψ-basic system is present as in benzamidine, benzaldoxime, and the Schiff's bases derived from benzaldehyde, salt-formation should produce very strong *m*-orientation owing to the direct transference [90] of part of the kationic charge to the atom adjacent to the ring. The examples mentioned give mainly *m*-nitro-derivatives on nitration in concentrated (or fuming) sulphuric acid,[91] but it is not necessary to assume, with Flürscheim and Holmes, that the *m*-directive power of *neutral* ·C⁚N is greater than that of ·C⁚O. A ψ-acidic system should act oppositely, and a phenylnitromethane should give smaller quantities of *m*-derivative in proportion as its ionisation is promoted :



(kation of ψ-base)



(anion of ψ-acid)

(II) *Transmission of Orienting Effects. The Direct Effect.*—In last year's Report a classification of orienting groups was given which was based on the possible effective combinations of two influences, namely, the inductive effect (±*I*), whereby the substituent permanently alters the electron-availability at each position in the aromatic nucleus by creating a permanent electric moment measurable as the molecular dipole moment, and the tautomeric effect (+*T*), which produces little permanent effect, but operates according to the instantaneous requirements of a suitably situated attacking reagent.[33] It is suggested [92] that the permanent electrochemical nature of the substituent will modify the electron availability at the various aromatic positions by a third mechanism, namely, by direct action through space (±*D*), although the operation of this mechanism seldom becomes obvious except when a decision is required between alternative substitutions nearly equally favoured by the inductive and the tautomeric effects. Since the genesis of the " direct " effect is thus the same as that of the inductive, it will follow the latter in sign and magnitude in its variation as between one directing group and another. Once originated, however, its distribution will depend on distance and will thus be, not in the order *op*>*m*, but in the order *o*>*m*>*p*.

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[88] J. W. Baker, K. E. Cooper, and C. K. Ingold, *loc. cit.*; B. Flürscheim and E. L. Holmes, *J.*, 1928, 2230; **A.**, 1126.

[89] *Ibid.*, p. 1280; **A.**, 782.

[90] *Ann. Reports*, 1927, **24**, 106, 115.

[91] R. Forsyth, V. K. Nimkar, and F. L. Pyman, *J.*, 1926, 800; **A.**, 1926, 611; O. L. Brady and B. E. M. Miller, *J.*, 1928, 338; **A.**, 414; B. Flürscheim and E. L. Holmes, *loc. cit.*

[92] C. K. Ingold and C. C. N. Vass, *ibid.*, p. 417; **A.**, 402; A. Lapworth and R. Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, No. 4, 1.

(a) *One orienting group.* The simplest application is to the ratio *o*-/*p*- for the introduction of a second substituent into a monosubstituted benzene, but illustrations must here be confined to cases in which the results cannot be confused with the effects either of steric hindrance or of the operation of special mechanisms such as those which complicate the substitutions of αβ-unsaturated benzene derivatives and the nuclear alkylation of phenols.[93] One such illustration is provided by the nitration of the phenyl[94] and benzyl[95] halides. The direct effect of the halogens should be a de-activating influence in the order F>Cl>Br>I, since the inductive effect is of this sign and in this order[79] (see under *b* above). The table below, which records the values of the ratio para-/½ ortho-, shows the strong depression of *o*-reactivity ascribed to the direct effect (—*D*) of the halogen in fluorobenzene, and the smaller and diminishing depressions exhibited by its analogues of higher and increasing molecular weight. It is natural that for the two benzyl compounds the ratio should be smaller than for their phenyl analogues, for not only will the direct effect over the aromatic nucleus be smaller as a whole in the benzyl series, but also the relative distances of the *o*- and *p*-positions from the halogen will be more nearly equal. Not only the differences between members of the same series, but also those between corresponding members of the phenyl and benzyl series, are in all cases in the opposite direction to those to which steric hindrance would be expected to give rise.

X =	F.	Cl.	Br.	I.
PhX	13·76	4·64	3·30	2·85
BzX	3·89	3·28	—	—

(b) *Two orienting groups.* A simple case relating to the further substitution of a disubstituted benzene arises when two similar *op*-directive groups are in the *m*-position to each other, and thus collaborate as regards their inductive and tautomeric effects, but clash in their direct effects, the stronger of which should therefore determine the orientation in the absence of disturbing influences. For example, the mixed *m*-dihalogenobenzenes should substitute mainly in the *p*-position to the smaller halogen, unless this orientation is inverted by the contrary action of steric hindrance. The nitration of three mixed *m*-dihalogenobenzenes has recently been investigated with the following results : [96]

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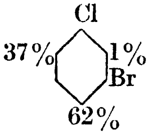
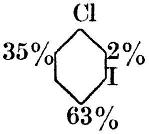
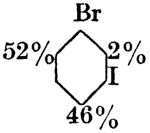
[93] For a discussion of these disturbances, see *Ann. Reports*, 1926, **23**, 140—143, and A. Lapworth and R. Robinson, *loc. cit.*

[94] A. F. Holleman and B. R. de Bruyn, *Rec. trav. chim.*, 1900, **19**, 189, 364; *A.*, 1900, i, 638; 1901, i, 318; *ibid.*, 1905, **24**, 140; *A.*, 1905, i, 515; *ibid.*, 1913, **32**, 134; *A.*, 1913, i, 844.

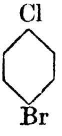
[95] C. K. Ingold and (Mrs.) E. H. Ingold, *loc. cit.*; (Miss) F. R. Shaw, *J.*, 1928, 2253.





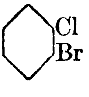


Definitely anomalous orientation, attributable to the operation of the direct effect, is rare, but a long-known instance is provided by A. F. Holleman's result for the nitration of *o*-chlorobromobenzene : [97]



$\left\{\frac{\text{Direction by Cl}}{\text{,,} \quad \text{,, Br}}\right. = \frac{45{\cdot}2}{54{\cdot}8}$

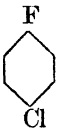
(Normal)



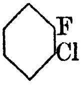
$\left\{\frac{\text{Direction by Cl}}{\text{,,} \quad \text{,, Br}}\right. = \frac{54{\cdot}5}{45{\cdot}5}$

(Anomalous)

It is easy to see that, whereas in the *p*-compound the direct effect will assist the other influences, in the *o*-compound it will oppose them, and in each case will favour substitution in the position furthest from the smaller halogen. In the bromoiodobenzenes, in which the direct effects are weaker, they are unable to cause an inversion in the *o*-compound of the normal orientation. In the fluorochloro-compounds, however, the direct effects (especially that of fluorine) are very strong, and the orientation in nitration is consequently normal but exaggerated in the *p*-compound, and strongly anomalous in its *o*-isomeride : [98]



$\frac{\text{Direction by F}}{\text{,,} \quad \text{,, Cl}} = \frac{20{\cdot}7}{79{\cdot}3}$



$\frac{\text{Direction by F}}{\text{,,} \quad \text{,, Cl}} = \frac{78{\cdot}7}{21{\cdot}3}$

(III) *Dynamics of Aromatic Substitution. Significance of Velocity Measurements, and Interpretation of " Nuclear Activation " in Terms of Energy.*—The work now to be described depends on the development of a method of nuclear substitution, which, from the point of view of accuracy of control and measurement, is a great advance on any previous attempt in this direction.

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[96] H. A. Mayes and E. E. Turner, *J.*, 1928, **691**; **A.**, 513.

[97] *Rec. trav. chim.*, 1915, **34**, 216; *A.*, 1915, i, 659.

[98] C. K. Ingold and C. C. N. Vass, *loc. cit.*; *ibid.*, p. 2262; **A.**, 1126.

(a) *Method for regulated halogenation.* The method is based on K. J. P. Orton and W. J. Jones's discovery [99] that the "rearrangement" of *N*-chloroanilides is dependent on the intermediate production of chlorine :

$$C_6H_5\cdot NClAc + HCl \underset{(a)}{\rightleftharpoons} C_6H_5\cdot NHAc + Cl_2 \longrightarrow C_6H_4Cl\cdot NHAc + HCl.$$

K. J. P. Orton and H. King [1] applied the reaction represented on the left to the production of a solution in acetic acid of chlorine in known concentration, and K. J. P. Orton and A. E. Bradfield recently developed the process further.[2] The methods recommended include the use of an aliphatic chloroamine, such as *N*-chloroacetamide, or an aromatic one with depressed nuclear reactivity, as, for instance, "dichloramine-T" or *N* : 2 : 4-trichloroacetanilide : the liberated chlorine is then wholly available for the chlorination of an added suitable aromatic compound. With these and many other chloroamines in glacial acetic acid, the equilibrium (*a*) lies almost entirely on the right, and since it is attained almost instantaneously, the addition of hydrochloric acid to a solution of a chloroamine results in the liberation of an exactly measured quantity of chlorine at the required moment. Further, as this chlorine disappears owing to nuclear chlorination of the aromatic compound it is replaced by an equivalent of hydrochloric acid, and hence (supposing that the chloroamine is in excess) by an equivalent of chlorine, the concentration of which, determined by the initial addition of hydrochloric acid, is thus automatically kept constant throughout the substitution. By this process, and various modifications of it, the velocities of chlorination of a number of anilides and phenol ethers have been determined. Solutions of iodine chloride have been similarly prepared from chloroamines and hydriodic acid and used for nuclear iodination.[3]

(b) *Chlorination of phenol ethers.* Difficulties of interpretation such as those due to basicity in the orienting group are here avoided, and a remarkably simple set of results has been obtained [4] for the chlorination at 20° in 99% acetic acid of a series of ethers of the type $RO\cdot C_6H_4\cdot X$(*o*- or *p*-). The figures are in the following table, in which concentrations are in g.-mols. per litre, and the bimolecular velocity coefficients (*k*) are expressed in terms of the same units of concentration, the unit of time being minutes :

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[99] *P.*, 1909, **25**, 196, 233, 305; *Brit. Assoc. Reports*, 1910, 85. Compare K. J. P. Orton, F. G. Soper, and G. Williams, *J.*, 1928, 998; **A.**, 628.

[1] *J.*, 1911, **99**, 1185.

[2] *J.*, 1927, 986; **A.**, 1927, 655.

[3] A. E. Bradfield, J. K. P. Orton, and I. C. Roberts, *J.*, 1928, 782; **A.**, 629.

[4] A. E. Bradfield and B. Jones, *ibid.*, p. 1006; **A.**, 628.

Velocity of Chlorination of $RO{\cdot}C_6H_4{\cdot}X$.

Concentration of chlorine		0·0075	0·0075	0·0075	0·020
,, of ether		0·0075	0·0225	0·0750	0·200
		Velocity coefficients (k).			
Group X.	Group R.				
Cl (p-)	CH_3–	1·323	1·226	—	—
,,	$CH_3{\cdot}CH_2$–	—	2·443	—	—
,,	$CH_3{\cdot}CH_2{\cdot}CH_2$–	—	2·756	—	—
,,	$(CH_3)_2CH$–	—	5·377	—	—
,,	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$–	—	2·723	—	—
,,	$C_6H_5{\cdot}CH_2$–	0·8783	0·8371	0·8054	—
,,	p-$C_6H_4Cl{\cdot}CH_2$–	—	0·4834	—	—
,,	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$–	—	0·1742	0·1828	—
,,	m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$–	—	0·2104	0·2068	—
Cl (o-)	CH_3–	—	4·441	—	—
,,	$CH_3{\cdot}CH_2$–	—	8·873	—	—
,,	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$–	—	0·6417	0·6586	—
CO_2H (p-)	CH_3–	0·4624	0·4440	0·4389	—
,,	$CH_3{\cdot}CH_2$–	0·9084	0·8774	0·8712	—
,,	$CH_3{\cdot}CH_2{\cdot}CH_2$–	—	0·9563	—	—
,,	$(CH_3)_2CH$–	2·053	1·975	—	—
,,	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$–	1·038	0·9633	—	—
,,	$C_6H_5{\cdot}CH_2$–	0·3232	0·3143	0·3002	—
NO_2 (p-)	CH_3–	—	—	—	0·002993
,,	$CH_3{\cdot}CH_2$–	—	—	—	0·005983
,,	$CH_3{\cdot}CH_2{\cdot}CH_2$–	—	—	—	0·006612

The velocity coefficients are seen to vary slightly with concentrations of the reactants, but it is shown that this makes no difference to the following analysis of the results :[5] First, let the velocities for each series of ethers with variable R and identical X be calculated in terms of the velocity for the methyl ether taken as 100; it then appears that the influence of R is independent of the nature of X :

						$\cdot CH_2{\cdot}C_6H_4{\cdot}A$.			
R =	Me.	Et.	Prα.	Buα.	Prβ.	A = H.	p-Cl.	m-NO_2.	p-NO_2.
X = p-CO_2H	100	198	215	221	444	70	—	—	—
p-NO_2...	100	200	221	—	—	—	—	—	—
p-Cl ...	100	199	225	222	439	67	39·4	17·2	14·2
o-Cl ...	100	199	—	—	—	—	—	—	14·4

Secondly, let the velocities for each series having variable X and identical R be computed in terms of the velocity for the p-carboxy-compound taken as 100; it transpires (as might, indeed, be inferred from the above) that the effect of X is independent of the nature of R :

X =	p-CO_2H.	o-Cl.	p-Cl.	p-NO_2.
R = Me	100	1000	276	0·674
Et	100	1010	278	0·682
Prα	100	—	288	0·691
Prβ	100	—	272	—
Buα	100	—	283	—
CH_2Ph	100	990	269	—

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[5] A. E. Bradfield and B. Jones, *J.*, 1928, 1006 ; **A.**, 628.

Before considering the broader significance of these results it may be noted that they place the groups in the proper theoretical order as regards their facilitation or inhibition of the nuclear substitution.[6]

(c) *Additive energy contributions.* The result of the above analysis may be expressed by the statement that, for this series of related compounds C_6H_4AB, the ratios of the velocities obtaining when $A = A_1, A_2, A_3, \ldots$ are independent of the nature of B, and *vice versa.* Further, since the equation for the critical energy increment is exponential in form ($k = \alpha e^{-E/RT}$), a *ratio* of velocities corresponds with a *difference* of energies, and the conclusion therefore suggests itself that the differences of the energies for compounds in which $A = A_1, A_2, \ldots$ are independent of the nature of B, and *vice versa,* or, in other words, that A and B additively and independently energise the position into which the new substituent will enter. This interpretation assumes, of course, that, of the two variables α and E, α remains constant, the variations in k being wholly accounted for by variations in E.

This conclusion, although the most obvious, is, as the authors point out, not the only possible one[7]; for, according to the modern theory of kinetic activation, the coefficient α of Arrhenius's equation *may* contain probability factors depending on the shape, orientation, and internal phase conditions of the molecule; wherefore α might vary from compound to compound in such a way as to give rise to the simple result obtained, even if (to take an extreme case) the energies of activation, E, were all equal. This, however, is not the correct view; for if it were, the ratio, k_1/k_2, of the k's for two substances at the same temperature would be α_1/α_2; that is, it would be independent of the temperature, which is found not to be the case. The remaining possibility, namely, that E, although variable, is compounded less simply than by addition, and that compensating changes in α cause the appearance of additivity, cannot at present be decided on the evidence. Further, it is not possible to determine the portion of the total energy E brought in by the reagent (Cl_2 in 99% acetic acid), although the implication is that it is constant in the cases considered.

The suggestion underlying this important work is clearly that the next step in the process of raising qualitative theories of reactivity to a quantitative status will consist in the determination of velocity coefficients, the translation of these into energies of activation, and the analysis of the latter into their component contributions; and even although it may not be possible *in general* [8] to add up energies at so much a group, the discovery that a large class of substances exists for which this simple procedure reproduces the experimental results with quite remarkable accuracy greatly brightens the prospect of advance along these lines.

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[6] In a later paper (A. E. Bradfield and B. Jones, *J.*, 1928, 3073) figures are given for two *iso*butyl ethers, namely, *p*-chlorophenyl *iso*butyl ether, $k = 2{\cdot}701$, and *p*-*iso*butoxybenzoic acid, $k = 0{\cdot}935$, which, although consistent with one another, are curiously enough, about 10% lower than values which might have been expected on the basis of the former results.

[7] *Idem, ibid.*

(IV). *Side-chain Reactivity.*—Although not strictly within the scope of aromatic substitution, this subject is conveniently dealt with here since its interest is of a related character.

The analysis of side-chain reactivity given in last year's Report was a duplex one, and during the year has been elaborated [9] into a four-fold classification according as the rate-determining process involves the following, or their equivalents :

(A_1) Separation of an anion.	Example : acid hydrolysis of benzyl halides.
(B_1) Separation of a kation.	Example : reduction of benzyl halides.
(A_2) Addition of an anion.	Example : alkaline hydrolysis of benzyl halides.
(B_2) Addition of a kation.	Example : formation of benzyl halides by halogenation.

A suitable subject for discussion here arises in connexion with instances in which it is sometimes difficult to determine whether the electrostriction of an external ion or intramolecular ionisation at a double linking is the important stage from this point of view.[10] In the case of styrene, the question, raised by F. Ashworth and N. Burkhardt [11] in connexion with the opposite modes of addition of thiophenol and hydrogen bromide, appears to be answerable as follows : Electron displacements in unsubstituted phenyl may be of either sign, and are tautomeric, and hence arise on demand from the reagent (pp. 121, 129); therefore, the phenomenon referred to merely means that the strongly basic anion (prone to co-ordinate) of weakly acidic thiophenol attacks before its kation, whereas the relatively inert anion of strongly acidic hydrogen bromide leaves its kation to initiate the attack (reaction must always commence at C_β because Ph absorbs the C_α charge):

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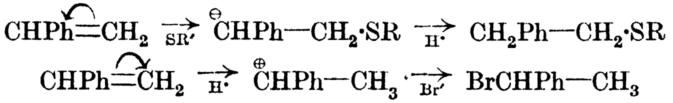
[8] Thus, accepting the constancy of a, a mutual effect due to two substituents occupying *the same* position in a side-chain appears discernible in the departure from exact geometric progression in the series $k_{\mathrm{OMe}} : k_{\mathrm{OEt}} : k_{\mathrm{OPr}^\beta} = 100 : 200 : 440$, which gives $E_{\mathrm{OEt}} - E_{\mathrm{OMe}} = 400$ g.-cals./g.-mol. and $E_{\mathrm{OPr}^\beta} - E_{\mathrm{OEt}} = 460$ g.-cals./g.-mol.; that is, there is a departure from additivity, or mutual effect, due to the two methyl groups in the *iso*propyl group, amounting to 60 g.-cals./g.-mol.

[9] C. K. Ingold and R. Rothstein, *J.*, 1928, 1217; **A.**, 747. For illustrations additional to those previously cited (*Ann. Reports*, 1927, **24**, 155) see *idem*, *ibid.*, the sections on prototropy and anionotropy (this vol., pp. 121 and 128), and two papers on the replacement of chlorine by iodine in the side chains of aromatic compounds (J. B. Conant, W. R. Kirner, and R. E. Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 488; *A.*, 1925, i, 492; G. M. Bennett and W. A. Berry, *J.*, 1927, 1676; **A.**, 1927, 871). As the last-named authors conclude, the reaction is facilitated by a recession of electrons from the point of attack; and this inference, although remarkable, collates many data not connected with aromatic substitution.

[10] That it is simplest to consider the effect of constitution on these processes *separately* does not imply that they are necessarily *separate in time*, *i.e.*, " stages " in the sense of " consecutive reactions " : they are regarded merely as absorbing separate portions of the critical energy.

[11] *Ibid.*, p. 1791; **A.**, 994.



$$\text{CHPh}{=}\text{CH}_2 \xrightarrow[\text{SR}']{} \overset{\ominus}{\text{C}}\text{HPh—CH}_2\cdot\text{SR} \xrightarrow[\text{H}^{\cdot}]{} \text{CH}_2\text{Ph—CH}_2\cdot\text{SR}$$

$$\text{CHPh}{=}\text{CH}_2 \xrightarrow[\text{H}^{\cdot}]{} \overset{\oplus}{\text{C}}\text{HPh—CH}_3 \xrightarrow[\text{Br}']{} \text{BrCHPh—CH}_3$$

A very different condition is revealed by K. Kindler's [12] experiments on the addition of hydrogen sulphide to substituted benzonitriles and the hydrolysis of substituted ethyl benzoates with aqueous-alcoholic alkali. In each case, the attack is obviously by an anion (SH′ in one case, and OH′ or OEt′ in the other), but in neither example is it this attack which determines the velocity under the conditions of temperature and concentration used. For the order of facilitation by substituents is found to be p-NH_2 > p-OMe > p-Me > m-Me > (H) > p-Cl > m-Cl > p-Br > m-Br > p-I > m-I > m-NO_2 > p-NO_2, which clearly indicates that electron-*release* from the nucleus facilitates reaction; wherefore the more difficult phase [13] (*i.e.*, the rate-determining phase) of each reaction is evidently the intramolecular ionisation ($\text{RC}\overset{\curvearrowright}{\equiv}\text{N}$ or $\text{EtO}\cdot\text{CR}\overset{\curvearrowright}{=}\text{O}$) of the intrinsically *very stable* groups of the cyano- and carboxy-types.

The constitutional stability of the cyano-group is doubtless due to the causes considered on p. 139, and that of carbethoxyl is accounted for by its internally-satisfied betaine structure discussed in a previous Report [14]; the latter condition does not, however, apply to aldehydes exhibiting considerable carbonyl reactivity, and here the facility of internal ionisation ($\rightarrow\text{C}\overset{\curvearrowright}{=}\text{O}$) must often be comparable with that of anion-addition (*e.g.* $\leftarrow\overset{\oplus}{\text{C}}\text{—}\overset{\ominus}{\text{O}} + \overset{\ominus}{\text{Cy}} \longrightarrow -\text{CCy—}\overset{\ominus}{\text{O}}$). In such a case electron-displacements which accelerate the first-mentioned phase will retard the second, and *vice versa*; and since in either case the more difficult phase determines the rate, substituents of both polar signs may depress it. Conditions of this nature are possibly present in A. Lapworth and R. H. F. Manske's study of the formation of substituted benzaldehyde cyanohydrins,[15] although it should be noted that the measurements here relate to equilibria, that is, to the *differences* of the energies, and energy increments, of the factors and products of the reactions. The energy differences being taken as measures of the affinity of the aldehydes for hydrogen cyanide, the effect on this affinity of *p*-substituents, for example, is not (as might be assumed from Kindler's work on esters and nitriles) represented by the *continuous* polar sequence

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[12] *Annalen*, 1926, **450**, 1; **A.**, 1927, 55.

[13] That which requires the greater portion of the critical energy of activation.

[14] *Ann. Reports*, 1926, **23**, 139.

[15] *J.*, 1928, 2533; **A.**, 1245.

$$\text{(Enhancement)}\ \overbrace{\text{NMe}_2>\text{OMe}>\text{Me}}>[\text{H}]>\text{Cl}<\text{NO}_2\ \text{(Depression)}$$

but, on the contrary, is expressed by a series having a maximum at the unsubstituted compound :

$$\text{(Maximum)}\ [\text{H}]\left\{\begin{array}{lllll} & >\text{Me} & & >\text{OMe}>\text{NMe}_2 & \text{(Depression)} \\ >\text{Cl} & & >\text{NO}_2 & & \text{(Depression)} \end{array}\right.$$

That is, substituents of both polar signs do, in this case, inhibit addition to the carbonyl group.

Of course, it is only in the case of a very special balance between the facility of the phases requiring electron-release and -restraint that the maximum will occur at the unsubstituted compound. That the optimum is not attained *exactly* at this point in the reaction under consideration is evident from Lapworth and Manske's investigation of *m*-substituted derivatives of benzaldehyde. Here, owing to the difficulty which attends the transmission of polar influences from the *m*-position, the effects of all groups of either polar sign are expected to be smaller; that is, the *m*-groups should furnish a range of effects differing by smaller intervals from that of hydrogen and should thus locate the optimum more precisely. The *continuous* theoretical polar sequence for *m*-groups, corresponding to that given above for the *p*-groups, is as follows (*m*-NMe_2 was not investigated) :

$$\text{(Enhancement)}\ \overbrace{\text{Me}}>[\text{H}]>\overbrace{\text{OMe}>\text{Cl}>\text{N}}\text{O}_2\ \text{(Depression)}$$

the difference from the *p*-sequence being that OMe should now function as a weak attractor of electrons ($-I$), since its tautomeric effect ($+T$) cannot operate from the *m*-position (p. 122). The sequence observed is

$$\text{(Maximum)}\ \text{Cl}\left\{\begin{array}{ll} & >\text{OMe}>[\text{H}]>\text{Me}\ \ \text{(Depression)} \\ >\text{NO}_2 & \end{array}\right.$$

so that the optimum is attained by the rather slight electron-attraction of *m*-chlorine.

Putting the *p*- and *m*-series together, it is now possible to understand the figures given by Lapworth and Manske as proportional to the energy-differences representing the affinities of the aldehydes for hydrogen cyanide [16] :

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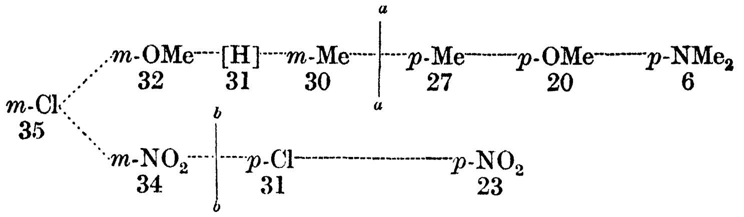
[16] Three special cases lie without the scope of this analysis : (i) *p*-OH (15) and *m*-OH (31), which find places to the right instead of to the left of the corresponding ·OMe groups; (ii) *o*-groups (other than ·OH), which enhance



The way in which the values for the *m*-substituents are seen to form a compact group (between *aa* and *bb*) which includes the values for the unsubstituted compound and the maximum, and is flanked on either side by the much more spread-out values for the *p*-substituents, testifies to the general truth of the above description of the process.[17]

Discussing possible explanations of their results, Lapworth and Manske suggested that, just as when the positive atomic nuclear charge increases in the series boron, carbon, nitrogen, and oxygen, stability in the quadricovalent state reaches a maximum at carbon and then declines, so also when the " positiveness " of the α-carbon atom of the benzene derivative is continuously increased by the use of nuclear substituents of increasing electron-affinity, stability in the cyanohydrin first rises to a maximum and then declines. This analogy is interesting but should be used with caution, for whereas, according to the usual view of the series of quadricovalent elements boron, carbon, nitrogen, and oxygen, the maximal stability at carbon is dependent on the unique neutrality of CR_4, the anion BF_4' loses an *anion* and the kation $NH_4^{\bullet}$ a *kation*, wherefore their decompositions, taken together, have only a partial resemblance to the decompositions, identical in type amongst themselves, of a pair of cyanohydrins with differently polar nuclear substituents.

A difficulty of different origin is furnished by the hydrolysis of acylated aromatic chloroamines. The hydrolysis constants of a number of these in 20% acetic acid have been determined by F. G. Soper and G. F. Smith,[18] with the following results *inter alia* :

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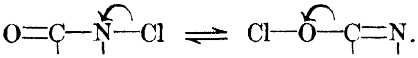
cyanohydrin formation (OMe 35, Cl 40, NO_2 42); and (iii) *o*-OH (24), which depresses cyanohydrin formation. Case (i) is probably attributable to ionisation, case (ii) partly to the direct effect, and partly to the effect of the external field on the concentration of cyanide ions near the aldehyde group, and case (iii) (compare Lapworth and Manske) to the formation of a ring with chelated hydrogen (Sidgwick).

[17] The Reporter thinks that the difference between this explanation and that of the authors is probably largely one of language, but the difficulty of the subject is such that he is compelled to try to explain the matter in the same terms as those in which he has succeeded in making it clear to himself.

[18] *Ibid.*, p. 138; **A.**, 249.

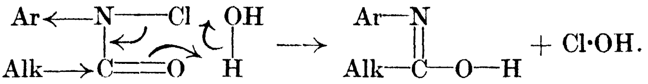
	$K_h \times 10^7$.		$K_h \times 10^7$.
N-Chloroformanilide ...	1·26	*N*-Chloroaceto-*p*-toluidide ...	3·48
N-Chloroacetanilide	6·70	*N*-Chloroacetanilide	6·70
N-Chloropropionanilide	7·5	*N*-Chloroaceto-*p*-chloroanilide	16·4
N-Chlorobutyranilide ...	7·0	*N*-Chloroaceto-*p*-nitroanilide...	324

Thus the remarkable fact emerges that, whereas modifications of structure which increase the electron-affinity of the aniline portion of the molecule also increase the hydrolysis (which is normal), modifications enhancing the electron-affinity of the acyl portion have the opposite result. This must mean that the N·Cl and C·O bonds are *both* concerned in the reaction, and in opposite senses. This conclusion is implied in the authors' explanation, which is that the chloroamines are tautomeric and hydrolyse in both forms :



$O{=}C{-}N{-}Cl \rightleftharpoons Cl{-}O{-}C{=}N$.

An alternative is that the process involves two-point attack by a water molecule, followed by decomposition in a cycle :



As the straight arrows show, not only electron-restraint in the arylamine portion of the molecule, but also electron-release in the acyl portion, will facilitate hydrolysis.

Triarylmethyls, Diaraminyls, and Aroxyls.

(Continued from *Ann. Reports*, 1924, **21**, 115.)

In the previous Report it was suggested that much of the confusion surrounding the triarylmethyls could be avoided by recognising the individuality of the three triphenylmethyls formed by neutral and ionic dissociation of hexaphenylethane (ⓝ = neutral, *i.e.*, non-ionic)

$$2Ph_3\overset{ⓝ}{C} \rightleftharpoons Ph_3C - CPh_3 \rightleftharpoons Ph_3\overset{\oplus}{C} + Ph_3\overset{\ominus}{C}.$$

The neutral radical is formed alone in non-ionising solvents, and the two ions together in ionising solvents; but the kation alone is present in the extensively studied solutions of triarylmethyl chlorides in liquid sulphur dioxide; and, it was suggested, the anion exists alone in solutions of potassium triphenylmethide (potassiotriphenylmethane) in liquid ammonia :

$$Ph_3CCl \rightleftharpoons Ph_3C^{\oplus} + Cl^{\ominus} \qquad Ph_3CK \rightleftharpoons Ph_3C^{\ominus} + K^{\oplus}.$$

Since 1924, the existence of the triphenylmethide anion in the ammonia solution has been confirmed, and some of its reactions have been investigated, although it is still much less well known than either the kation or the radical.

(a) *The Triphenylmethide Anion.*—Unlike the kation and the radical, which are both yellow, the anion is red, and red solutions of calcium, sodium, and potassium triphenylmethide in liquid ammonia have been studied.[19] The last two salts have been obtained in the solid state, but only the potassium salt is stable at the ordinary temperature. It is formed by direct neutralisation (in the sense appertaining to reactions in liquid ammonia) of potassamide by triphenylmethane :

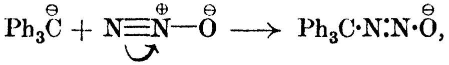
$$Ph_3CH + NH_2^{\ominus} \longrightarrow Ph_3C^{\ominus} + NH_3.$$

Triphenylmethane is therefore an acid (compare the equation for the neutralisation of an acid by hydroxide ions in water :

$$R{\cdot}CO_2H + OH^{\ominus} \longrightarrow R{\cdot}CO_2^{\ominus} + H_2O).$$

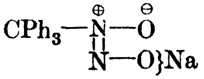
It is, however, a *very* weak acid, even according to the displaced scale of acidity appropriate to liquid ammonia solutions, for the potassium salt is slightly ammonolysed (the reverse reaction) and the sodium and calcium salts are considerably so. As a weak acid, the hydrocarbon is naturally liberated from its salts by the addition of the strong acid ammonium chloride (just as acetic acid would be liberated from sodium acetate in water by the addition of the strong acid hydronium chloride, that is, hydrochloric acid, OH_3Cl). Final proof of the electrovalent character of potassium and sodium triphenylmethide is furnished by the observation that their equivalent conductivity is as high as 64 units in 0·05*N*-solution.

Sodium triphenylmethide reacts with nitrous oxide, giving sodium triphenylmethanediazotate, $CPh_3{\cdot}N{:}N{\cdot}ONa$.[20] The reaction, which may be formulated

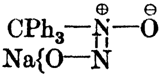


$$Ph_3\overset{\ominus}{C} + N{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{O} \longrightarrow Ph_3C{\cdot}N{:}N{\cdot}\overset{\ominus}{O},$$

is analogous to a diazo-coupling, and there can be little doubt but that diazonium salts would react similarly. The neutral radical nitric oxide, which always forms 1 : 1-additive compounds with (odd-electron) neutral radicals, reacts in two stages with the (even-electron) anion, giving a diazotate-oxide, existing in *syn-* and *anti*-forms : [21]



$$\begin{array}{l} CPh_3{-}\overset{\oplus}{N}{-}\overset{\ominus}{O} \\ \qquad\;\; \| \\ \qquad\;\; N{-}O\}Na \end{array}$$



$$\begin{array}{r} CPh_3{-}\overset{\oplus}{N}{-}\overset{\ominus}{O} \\ \| \quad\;\; \\ Na\{O{-}N \quad\;\; \end{array}$$

Ionising halogen compounds, such as triphenylacetyl chloride and chloromethyl ether, yield the expected products, $CPh_3{\cdot}CO{\cdot}CPh_3$ and $CPh_3{\cdot}CH_2{\cdot}O{\cdot}CH_3$.[21]

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[19] C. A. Kraus and R. Rosen, *J. Amer. Chem. Soc.*, 1925, **47**, 2739; **A.**, 1926, 57.

[20] W. Schlenk and E. Bergmann, *Annalen*, 1928, **464**, 1; **A.**, 1040.

[21] *Idem, ibid.*

(b) *Stability of the Triarylmethyl Ions and Radicals.*—A view with regard to the stability of triarylmethyls has recently been advanced [22] and may be reproduced here, since it will be of use in reviewing the further developments in the chemistry of these substances.

It has already been noted (pp. 121, 129) that aryl groups possess the remarkable property (probably shared to some extent by vinyl groups) of activating *both* prototropic and anionotropic three-carbon systems; that is, they are able, by tautomeric electron-displacements of either sign called into being according to the requirements of the system, to absorb an electric charge of either sign produced by ionisation on an attached atom. This explains, not only the effect of the system of aryl groups in hexa-arylethanes in simultaneously stabilising the two ions of opposite sign formed by the *ionic* dissociation of an ethane derivative, but also the power of the groups to confer stability on the neutral radical (electron septet); for the methyl carbon in the neutral radical is simultaneously affected by two factors, normally conducive to instability, which are identical in type with those present separately in the two ions, namely, the incompleteness of the octet, which applies also to the positive ion, and the incompleteness of the sharing, which applies also to the negative ion; and a system of groups which can successfully combat *both* these factors of instability separately can also combat them together. The process giving stability to the neutral radical may be expressed thus: electron-release from the aryl groups partly repairs the disrupted octet, and, incidentally, the disrupted duplet; the unshared pair, thus partly formed, is partly shared by the aryl groups.

Before considering to what extent this view simplifies the chemistry of free radicals, it is desirable to review the external evidence relating to it. The capacity of aryl groups for stabilising positively and negatively charged tercovalent carbon has already been amply illustrated in the section on tautomerism (pp. 121, 129), and nothing further need be added here. External evidence concerning the ability of aryl groups to confer stability on neutral radicals containing tercovalent carbon is afforded by recent studies on the alkali-metal derivatives of aromatic hydrocarbons, imines, and ketones.

W. Schlenk and E. Bergmann have prepared and studied a large number of compounds formed by the addition of sodium and lithium to olefinic hydrocarbons.[23] In the course of this work they never found (except in one case for which a special reason exists) the metallic atom in combination with a carbon atom unless at least one aryl group was also attached to the same carbon atom. This fact, which is obviously related to the exclusively terminal addition of hydrogen to the inter-nuclear carbon chains in the reduction of the hydrocarbons $C_6H_5{\cdot}CH{:}CH{\cdot}[CH{:}CH]_n{\cdot}CH{:}CH{\cdot}C_6H_5$ ($n = 0, 1, 2, 3$),[24] shows that the free electron associated with an atom of sodium adds initially to the carbon atom attached to aryl. This initial product must necessarily be a free radical (analogous to a ketyl). Now Schlenk and Bergmann found, furthermore, that the subsequent course of the reaction depends on whether or not aryl groups in sufficient number are attached to the non-ionic tercovalent carbon atom. If they are not, as in the reaction of *as*-diphenylethylene, then polymerisation, of the type familiar in pinacol and similar reductions, will at once occur :

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[22] H. Burton and C. K. Ingold, *J.*, 1928, 907.

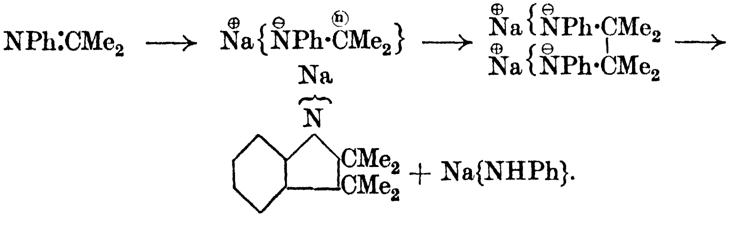
[23] *Annalen*, 1928, **463**, 1; **A.**, 1031.

$$CPh_2{:}CH_2 \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{C}Ph_2{\cdot}\overset{\text{ⓝ}}{C}H_2\} \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{C}Ph_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\ominus}{C}Ph_2\}\overset{\oplus}{Na}.$$

If, on the other hand, aryl groups are present to stabilise the septet, it can persist without polymerisation, although ultimately a second encounter with the sodium surface causes it to do precisely what neutral triphenylmethyl would do in similar circumstances, namely, undergo conversion into the sodium alkide :

$$CPh_2{:}CPh_2 \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{C}Ph_2{\cdot}\overset{\text{ⓝ}}{C}Ph_2\} \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{C}Ph_2{\cdot}\overset{\ominus}{C}Ph_2\}\overset{\oplus}{Na}.$$

Similarly anils[25] derived from aliphatic ketones take up only one atom of sodium and then polymerise ; in the case of acetoneanil the pinacol-like polymeride subsequently loses an anilide ion, the isolated product being an indoline :



The anil from acetophenone, on the other hand, takes up two atoms of sodium :

$$NPh{:}CMePh \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{N}Ph{\cdot}\overset{\text{ⓝ}}{C}MePh\} \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{N}Ph{\cdot}\overset{\ominus}{C}MePh\}\overset{\oplus}{Na}.$$

Furthermore, whereas the ketyls[26] derived from purely aliphatic ketones have never been caused to take up a second metallic atom, benzophenone and phenyl *p*-diphenylyl ketone react with sodium in two distinct stages thus :

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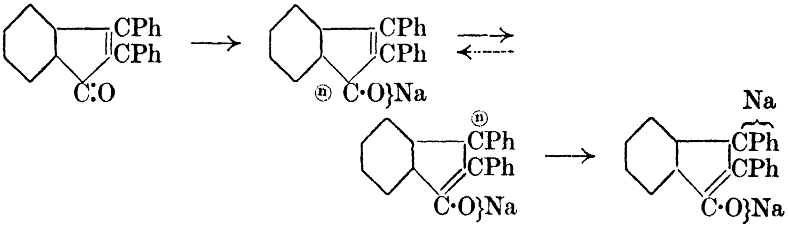
[24] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 1928, **11**, 123; **A.**, 281.

[25] W. Schlenk and E. Bergmann, *Annalen*, 1928, **463**, 281; **A.**, 1039.

[26] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, 1914, **47**, 486; *A.*, 1914, i, 396; W. Schlenk and E. Bergmann, *Annalen*, 1928, **464**, 22; **A.**, 1041.

$$O{:}CAr_2 \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{O}{\cdot}\overset{\textcircled{n}}{C}Ar_2\} \longrightarrow \overset{\oplus}{Na}\{\overset{\ominus}{O}{\cdot}\overset{\ominus}{C}Ar_2\}\overset{\oplus}{Na}.$$

The reaction of 2 : 3-diphenylindone is interesting. Here the ketyl must evidently be electromeric, and it is found that the electron-septet establishes itself on the γ-carbon atom to which two aryl residues are attached, and not on the α-atom which bears only one; a second atom of sodium, therefore, is taken up, but, in this case, on the γ-carbon atom, as is shown by the formation 2 : 3-diphenyl-1-hydrindone-3-carboxylic acid on treatment of the disodium compound with carbon dioxide :



(c) *Triarylmethyl Radicals.*—Returning now to the chemistry of the hexa-arylethanes, two direct consequences of the hypothesis described in the foregoing section may be mentioned as assisting in the elucidation of recent observations.

The first is that polynuclear aromatic systems should act more powerfully than phenyl in promoting the dissociation of hexa-arylethanes (stabilising the radical), because the rings of a polynuclear group which are more distant from the ethane carbon atom will " back up " the nearer ring in both its functions of electron-release and -reabsorption. A theoretical sequence can be constructed, such as 9-phenanthryl>α-naphthyl>β-naphthyl>*p*-diphenylyl>*m*-diphenylyl>phenyl, and this has been verified to the extent represented by α-naphthyl>β-naphthyl>*p*-diphenylyl>phenyl by the work of Gomberg and Schlenk.[27] The same view accommodates the transmission of the effect of aryl (with damping) through an intermediate single or double linking, as illustrated by the marked stability of the free radicals pentaphenylethyl,[28] $CPh_3{\cdot}CPh_2\textcircled{n}$, and tetraphenylallyl,[29] $CPh_2{:}CH{\cdot}CPh_2\textcircled{n}$. It also suggests that ethylenic linkings themselves may contribute to the effect (compare p. 152), and this may also be a circumstance of some importance in relation to the quite remarkable stability of tetraphenylallyl. Possibly the steric factor plays a part in the case of pentaphenylethyl.

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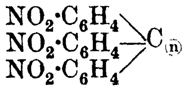
[27] M. Gomberg and F. W. Sullivan, *J. Amer. Chem. Soc.*, 1922, **44**, 1829; *A.*, 1922, i, 929; W. Schlenk, T. Weikel, and A. Herzenstein, *Annalen*, 1910, **372**, 1; *A.*, 1910, i, 236.

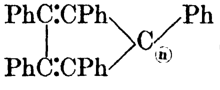
[28] W. Schlenk and E. Mark, *Ber.*, 1922, **55**, [*B*], 2285, 2299; *A.*, 1922, i, 1002, 1003.

[29] K. Zeigler, *Annalen*, 1923, **434**, 34; *A.*, 1924, i, 308.

The second deduction follows from the consideration that the triphenylmethyl anion is obviously much less stable than the kation.[30] For the assumption is that stability in a neutral radical is dependent on the presence of a condition, the efficacy of which is indicated by its ability to stabilise, not only the corresponding kation, but also the anion; wherefore the efficacy of phenyl in stabilising neutral triphenylmethyl is evidently limited primarily by its capacity to perform that function by which also it confers stability on the anion. Therefore, within wide limits, the introduction of any substituent calculated to increase the stability of the anion should also increase the stability of the neutral radical. For example, the introduction of *m*-orienting groups ($-I$ effect) should act as described, and should operate more powerfully from the *p*-position than from the *m*-position.

An interesting example of this effect is provided by the radical *pp'p''*-trinitrophenylmethyl, recently isolated by K. Zeigler and E. Boye.[31] The magnitude of the effect of the three nitro-groups is indicated by the greatly increased stability of the dark blue anion, which can exist undecomposed even in alcohol, and the neutral radical possesses so little tendency to associate that it can be isolated in the free state as deep green needles.

(deep green) 

 (reddish-violet)

Pentaphenyl*cyclo*pentadienyl affords another illustration.[32] Here the electron-affinity of the *cyclo*pentadiene ring itself (p. 120) provides the system as a whole with an added capacity for electron-

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[30] A striking illustration of the stability of the kation is afforded by the observation (C. A. Kraus and R. Rosen, *loc. cit.*) that triphenylmethyl chloride is soluble in liquid ammonia with only slight, and reversible, conversion into triphenylmethylamine (ammonolysis):

$$Ph_3\overset{\oplus}{C} + \overset{\ominus}{Cl} + NH_3 \rightleftharpoons Ph_3C{\cdot}NH_2 + \overset{\oplus}{H}\ (i.e.,\ \overset{\oplus}{N}H_4) + \overset{\ominus}{Cl}$$

The little which does take place is inhibited by the addition of ammonium chloride [just as the hydrolysis of ammonium chloride would be inhibited by the addition of hydrochloric acid:

$$N\overset{\oplus}{H}_4 + \overset{\ominus}{Cl} + H_2O \rightleftharpoons NH_4{\cdot}OH + \overset{\oplus}{H}\ (i.e.,\ \overset{\oplus}{O}H_3) + \overset{\ominus}{Cl}].$$

[31] *Annalen*, 1927, **458**, 248; **A.**, 1928, 59.

[32] K. Zeigler and B. Schnell, *ibid.*, 1925, **445**, 266; **A.**, 1926, 57.

absorption. Actually, the anion was not investigated in this case, but the free radical was isolated as reddish-violet crystals, and could not be caused to associate.

Some of these instances are difficult to reconcile with Flürscheim's theory relating to the free radicals.

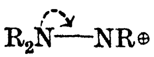
op-Orienting groups of the $-I + T$,type with a considerable $-I$ effect (*e.g.*, OMe, Cl) should act in the same way, and groups of the $+I$ type (*e.g.*, alkyl) in the opposite way.

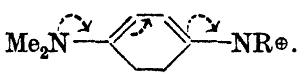
(d) *The Diaraminyls and Diarylacylhydrazyls.*—The increase of anionic stability corresponding with increasing central nuclear charge in the series CH_3, NH_2, OH—illustrated by the stability of the anion of sodamide in liquid ammonia but not in water—naturally leads, in the application of Burton and Ingold's mechanism to the diaraminyls (" diaryl nitrogens "), to consequences which differ in certain important respects from those relating to triarylmethyls. For in any relatively simple case the ability of bicovalent nitrogen to sustain an *anionic* charge is assured; it is in its support of a *kationic* charge that it requires external assistance in order to produce that balanced capacity for electron-absorption and -release on which, according to hypothesis, the stability of the radical depends. Wherefore, within wide limits, *op*-orienting groups should increase radical stability; and they should do so in proportion to their *op*-directive power. This agrees with the order of radical stability established by Wieland,[33] namely,

$$(H{\cdot}C_6H_4)_2N < (p\text{-}MeO{\cdot}C_6H_4)_2N < (p\text{-}Me_2N{\cdot}C_6H_4)_2N.$$

Other conclusions, which have not yet been verified, are that the effect of such substituents should be diminished if they are in the *m*-position, and that the relative effects of unsubstituted polynuclear groups (except indenyl, etc.) should be as they are in the triarylmethyl series.

The hydrazyls are in a different case again. Here the kationic stability is expected to be very much greater, because, in the hydrazyl kation, the breach in the octet of one nitrogen atom can be partly filled by the unshared pair of the other atom, which thereby approaches the ammonium (quadricovalent) condition. Indeed, the process is merely a simpler form of what was assumed to occur in the *p*-dimethylamino-compound considered above :





Thus the intrinsic stability of nitrogen both in its amide (negative, bicovalent) and ammonium (positive, quadricovalent) forms, leads, in the hydrazyls, to a singularly even balance between their capacities for electron-restraint and -release; wherefore the way in which to increase the stability of the neutral hydrazyl radical by substitution is to introduce (within limits) either an electron-releasing group or an electron-restraining group, or, better still, *a group of each kind.* This is what Goldschmidt[34] did in his study of the acyldiarylhydrazyls, NArAc·NAr⊙, and his order of radical stability, namely, acetyldiphenyl<benzoyldiphenyl<acetyldi-*p*-tolyl<benzoyldi-*p*-tolyl<acetyldi-*p*-dimethylaminophenyl, and, further, benzoyldiphenyl<picryldiphenyl, which appeared so puzzling in 1924, is now seen exactly to correspond with what might have been anticipated [order of electron-restraint (from strengths of acids R·OH), acetyl<benzoyl<picryl; order of electron-release (from strengths of bases R·NH$_2$), phenyl<*p*-tolyl<*p*-dimethylaminophenyl].

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[33] *Ann. Reports*, 1924, **21**, 119.

(e) *The Aroxyls.*—Owing to the great anionic and small kationic stability of unicovalent oxygen, the latter condition must always set the limit to the stability of neutral aroxyls. Actually the only compounds in which perceptible stability in the free radical has been reported contain a strongly *op*-orienting group in the *o*-position to the univalent oxygen atom. The most recent examples are 10-bromo- and 10-phenoxy-9-phenanthroxyl.[35]

The Bile Acids.

(Continued from *Ann. Reports*, 1927, **24**, 128.)

(a) *Occurrence.*—One more bile acid has now to be added to the list of those whose constitutions have been elucidated so far as rings I, II, and III and the carboxylated side-chain are concerned. The new member of the series, β-phocæcholic acid, is furnished by the walrus, and by certain seals, in the form of salts of its amide with taurine.[36] The acid is a trihydroxycholanic acid, and is therefore isomeric with cholic acid; so far as is known, it is unique amongst the bile acids in that it contains a hydroxyl group in the carboxylated side-chain.

Cholic acid has been obtained from the bile of antelopes, and deoxycholic acid from the same source, and also from deer.[37] The complete list of known naturally occurring hydroxycholanic acids is therefore as follows :

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[34] *Ann. Reports*, 1924, **21**, 120.

[35] S. Goldschmidt, A. Vogt, and M. A. Bredig, *Annalen*, 1925, **445**, 123; *A.*, 1925, i, 1434; compare *Ann. Reports*, 1924, **21**, 121.

[36] O. Hammarsten, *Z. physiol. Chem.*, 1909, **61**, 454; 1910, **68**, 109; *A.*, 1909, ii, 819; 1910, ii, 879.

[37] A. Windaus and A. van Schoor, *ibid.*, 1928, **173**, 320; **A.**, 639.

Acid.	Synonyms.	Positions of OH-groups.	Sources.
Lithocholic	—	3	Man, ox.
Deoxycholic	Choleic	3, 7	Man, ox, goat, sheep, deer, antelope.
Chenodeoxycholic	Anthropodeoxycholic	3, 12	Man, ox, goose, hen.
Hyodeoxycholic	Hyocholic	3, 13	Pig.
Cholic	Cholalic	3, 7, 12	Man, ox, goat, sheep, antelope.
β-Phocæcholic	*iso*Cholic, *iso*Cholalic	3, 12, 23	Walrus, seal.

The bile of deer contains, in addition, four specific acids,[38] one of which appears to be a tetrahydroxycholanic acid, and these must now be included in the list—which also contains α-phocæcholic acid from the walrus, ursocholic acid from the polar bear, and fellic acid from man—of the bile acids at present awaiting detailed investigation.

(b) β-*Phocæcholic Acid.*[39]—This trihydroxymonobasic acid, $C_{24}H_{40}O_5$, on oxidation with permanganate, yields a dihydroxymonobasic acid with one carbon atom less, $C_{23}H_{38}O_4$. The degradation can be represented only in one way, namely,

$$[C_{22}H_{37}O_2]\cdot CH(OH)\cdot CO_2H \longrightarrow [C_{22}H_{37}O_2]\cdot CO_2H,$$

whence it shows that one hydroxyl group is adjacent to the carboxyl group.

The dihydroxy-acid, $C_{23}H_{38}O_4$, when fully reduced, by first oxidising it with chromic acid to the diketo-acid, $C_{23}H_{34}O_4$, and then reducing the carbonyl groups to methylene groups by Clemmensen's method, gives a monobasic acid, $C_{23}H_{38}O_2$, identical with Wieland, Schlichting, and Jacobi's norcholanic acid.[40] This proves that β-phocæcholic acid is a cholanic acid derivative, with a hydroxyl group attached to C_{23}.

The positions of the two remaining hydroxyl groups are shown by the fact that β-phocæcholic acid on oxidation with sodium hypobromite yields the lactone, $C_{24}H_{36}O_7$, of a dihydroxytribasic acid; that is, it gives a " biliobanic " acid. In the bile acid series, this reaction is definitely characteristic [41] of compounds containing hydroxyl groups in positions 3 and 12; the lactone may be termed phocæbiliobanic acid or 23-hydroxychenodeoxybiliobanic acid.[42] That the 23-hydroxy-group remains undisturbed during the formation of this acid is shown by the fact that on further oxidation it behaves just as phocæcholic acid does in the permanganate oxidation mentioned above; that is, it loses one atom of carbon from the side chain and yields a lactonic acid, $C_{23}H_{34}O_6$, which may be called norchenodeoxybiliobanic acid. The formulæ below illustrate these transformations.

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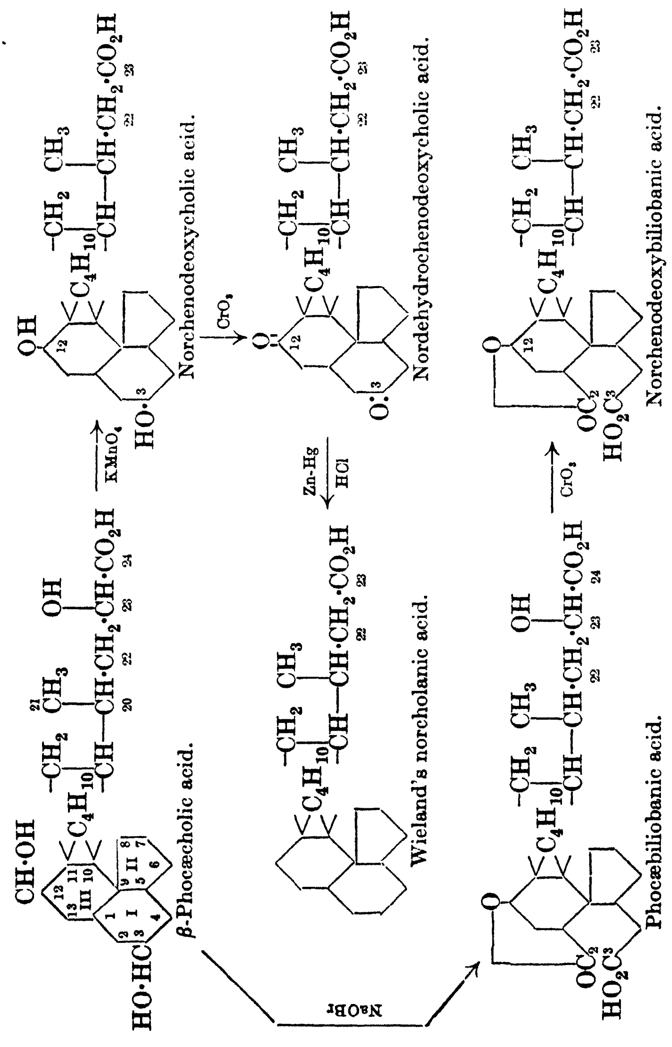
[38] A. Windaus and A. van Schoor, *Z. physiol. Chem.*, 1928, **173**, 320; **A.**, 639.

[39] *Idem, ibid.*

[40] *Ann. Reports*, 1926, **24**, 130.

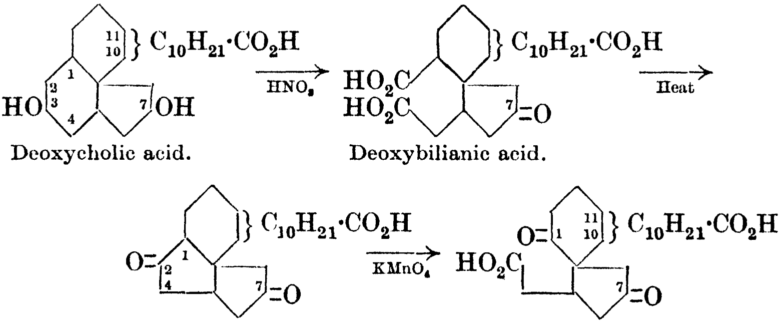
[41] Doubtless it would be desirable to have independent confirmation of the locations of the 3- and 12-hydroxy-groups by methods depending on direct identification.

[42] *Ibid.*, p. 140.


β-Phocæcholic acid.
KMnO₄
Norchenodeoxycholic acid.
CrO₃
Nordehydrochenodeoxycholic acid.
Zn-Hg
HCl
Wieland's norcholanic acid.
NaOBr
Phocæbiliobanic acid.
CrO₃
Norchenodeoxybiliobanic acid.

(c) *The Fourth Ring of Cholane.*—The conclusions with regard to ring (IV) which follow from the experimental evidence summarised in last year's Report may be expressed thus :—(i) Ring IV is attached to Ring III at C_{10} and C_{11}. (ii) Ring IV contains a tertiary carbon atom which carries the carboxylated side chain of the bile-acids. (iii) Adjacent to this carbon atom, there is, in Ring IV, a secondary carbon atom. (iv) Ring IV is a *cyclo*pentane ring, and therefore bears, at one or more of the three carbon atoms other than those carrying the carboxylated side chain and the adjacent pair of hydrogen atoms, three carbon atoms in the form of alkyl groups (trimethyl, methylethyl, or *n*- or *iso*-propyl).[43] It remained to locate the carboxylated side chain, and to identify and locate the 3C-alkyl group or groups. This year the problem has been advanced to the extent that one of the three alkyl carbon atoms has been identified as a methyl group, and its position determined to a degree of approximation which greatly limits the number of possible cholane formulæ.

The starting point of the new investigation[44] is a diketodibasic acid obtained from pyrodeoxybilianic acid. The latter, which is obtained from naturally occurring deoxycholic acid, *via* deoxybilianic acid, on oxidation *with nitric acid* yields norcholoidanic acid, the pentabasic acid formed by fission between C_2 and C_4;[45] on the other hand, when *permanganate* was used, fission occurred between C_1 and C_2, and the product was the diketodibasic acid, $C_{23}H_{34}O_6$:


$C_{10}H_{21}\cdot CO_2H$
11
10
1
2
3
4
7
HO
OH
HNO_3
HO_2C
HO_2C
$C_{10}H_{21}\cdot CO_2H$
7
=O
Heat
$C_{10}H_{21}\cdot CO_2H$
O=
1
2
4
7
=O
$KMnO_4$
$C_{10}H_{21}\cdot CO_2H$
O=
1
11
10
HO_2C
7
=O

Deoxycholic acid. Deoxybilianic acid.

Pyrodeoxybilianic acid. $C_{23}H_{34}O_6$.

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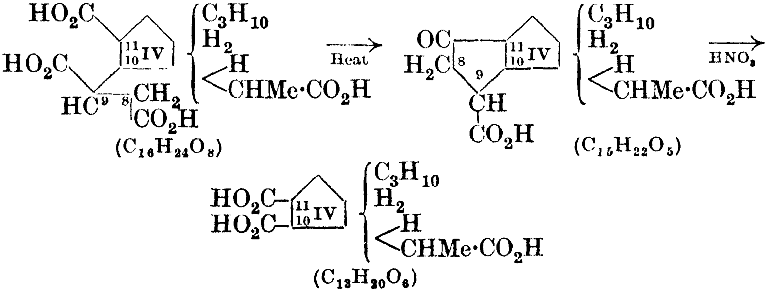
[43] Owing to an oversight, the Reporter omitted to mention the most important piece of evidence on this point, namely, that ætiobilianic acid, the dibasic acid obtained by Wieland, Schlichting, and Jacobi by removing the carboxylated side chain of cholanic acid and opening ring IV by oxidation, on thermal decomposition yields, not a "pyro-compound" (*i.e.*, a ketone), but an internal anhydride. Ætiobilianic acid is, therefore, a glutaric acid and not an adipic acid, wherefore ring IV must be a *cyclo*pentane ring. In the reference at the foot of p. 130, "**A.**, 1926" should read "**A.**, 1927."

[44] H. Wieland and F. Vocke, *Z. physiol. Chem.*, 1928, **177**, 68; **A.**, 1007.

[45] *Ann. Reports*, 1927, **24**, 138.

This acid, on oxidation with nitric acid, underwent extensive degradation, yielding two acids which are of considerable significance from the constitutional point of view.

The first of these was a tetrabasic acid, $C_{16}H_{24}O_8$, previously described by H. Wieland and O. Schlichting.[46] On heating, it yielded a keto-dibasic acid, $C_{15}H_{22}O_5$, which on oxidation with nitric acid gave a tribasic acid, $C_{13}H_{20}O_6$; the last on heating gave an anhydro-acid, $C_{13}H_{18}O_5$. These compositions, which have been fully confirmed by the preparation of numerous derivatives, can be accounted for consistently with already established conclusions, only on the assumption that the ring which survives oxidation in the formation of the tetrabasic acid is ring IV. This confirms the view that ring IV is not hydroxylated in any of the known hydroxycholanic acids, and thus clears up the only previously doubtful point[47] relating to rings I, II, and III, which otherwise would have affected any further conclusions which might be drawn with regard to ring IV and its attachments. The course of the degradation to the C_{13}-acid (which, incidentally, is optically active) may be expressed in the following scheme, in which an obvious alternative formula for the pyro-acid, $C_{15}H_{22}O_5$, has been omitted :



The second acid was a tribasic acid, $C_7H_{10}O_6$, which on heating gave α-methylglutaric acid, and was thereafter identified by synthesis as *n*-butane-αγγ-tricarboxylic acid, $HO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(CO_2H)_2$. This important discovery proves that the cholanic acid molecule contains a methyl group attached to a quaternary carbon atom. So much of the cholane skeleton is now known that, disregarding the unlikely possibility that the oxidation of a *gem*-dialkyl group attached to ring IV converts one alkyl group into carboxyl and leaves the other, a methyl group, intact, there remain C_{10} and C_{11} as the only possible positions for the newly identified methyl group; and in either case it is necessary that an adjacent carbon atom should be secondary in order to account for the β-methylene group in the *n*-butane acid.[48] The last condition limits the number of ways in which the *n*-butane acid could arise by degradation of the C_{23}-acid to three, one of which assumes a 10-methyl group, whilst either of the other two remains open if the methyl group occupies position 11 :

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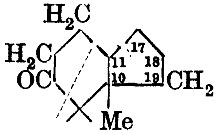
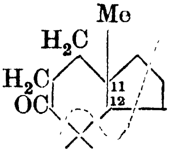
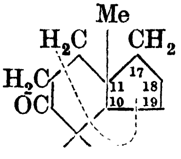
[46] *Z. physiol. Chem.*, 1924, **138**, 276; *A.*, 1924, i, 857.

[47] *Ann. Reports*, 1927, **24**, 137.







These alternatives being combined with the conclusion that the carboxylated side chain in cholanic acid is attached to a tertiary carbon atom adjacent to a methylene group, the number of possible cholanic acid formulæ is reduced to twenty, as follows :

Quaternary Me.	Carboxylated chain.	Alkyl groups, Me_2 or Et.	No. of alternatives.
10	17	11	1
10	18	11 and/or 17	4
11	17	10 and/or 19	4
11	18	10 and/or (17 or 19)	7
11	19	10 and/or 17	4

Strictly, the argument cannot be carried beyond this point; but Wieland and his collaborators incline to the last eleven possibilities (especially the last four), partly because the carboxylated side chain in the bile acids can apparently interact with groups in ring II,[47] and less difficulty is experienced in formulating these reactions if the side chain is placed at C_{18} or C_{19}, and partly because it is simpler to think of the two methylene groups in the *n*-butane acid as pre-existing in cholanic acid, rather than that one is formed by decarboxylation of a malonic acid group during oxidation, and, if the quaternary methyl group were at C_{10}, the simpler view would be tenable only if the carboxylated side chain were at C_{17}, which is considered improbable for the reason stated. Independently of these arguments, it is interesting to notice that one of the last eleven alternatives, namely, the 11-19-10-combination, is unique amongst the whole twenty in that it corresponds to a cholesterol skeleton divisible into a farnescene chain (thick lines, left formula), and a residue which may be regarded either as a C_6-ring and two C_3-groups, or as two normal C_6-chains (thick lines, right formula) in head-to-tail combination with each other and the farnescene chain. The following are, therefore, provisional representations of cholesterol and cholic acid, suggested by the assumption that their mode of biosynthesis is dependent jointly on those of the terpenes and sugars :[49]

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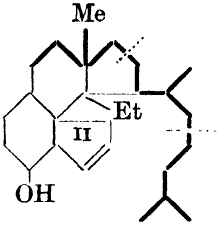
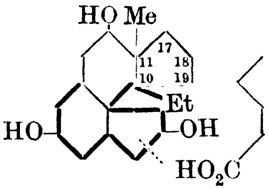
[48] The carbon atom of cholanic acid, which becomes the α-carbon atom of the *n*-butane acid, *need* not also be secondary, because it could become so during the oxidation by decarboxylation of a malonic acid residue.



Cholesterol.



Cholic acid.

In conclusion, I wish gratefully to acknowledge that in preparing this series of Reports on the Homocyclic Division of Organic Chemistry I have throughout enjoyed the collaboration of my wife, whose labours in compilation, and judgment in matters requiring discussion have greatly facilitated an arducus duty.

C. K. INGOLD.

PART III.—HETEROCYCLIC DIVISION.

Oxygen Ring Compounds.

MOST of the interesting work which has been carried out in this branch of chemistry during the year has been concerned with the structure of natural products.

Among the naturally occurring hydroxycoumarins, fraxetin, long known to be the monomethyl ether of a trihydroxycoumarin, the glucoside of which is fraxin from the bark of *Fraxinus excelsior*, has now been shown by F. Wessely and E. Demmer[1] to have the structure (I). Its dimethyl ether, on treatment first with sodium methoxide and then with methyl iodide, yielded a methyl tetramethoxycinnamate which gave 2 : 3 : 4 : 5-tetramethoxybenzoic acid on hydrolysis and subsequent oxidation, and by a similar process its diethyl ether gave an acid which was shown to be 2 : 5-dimethoxy-3 : 4-diethoxybenzoic acid.

Anthocyanins.—Since the earlier, well-known syntheses of the anthocyanidins through their methyl ethers require considerable practice and technique, and are likely to lead to impure products during the demethylation process, experiments have been carried out with a view to find a modified procedure which would lead to more certain results. The *O*-monobenzoylphloroglucinaldehyde which results from the monobenzoylation of phloroglucinaldehyde by the Schotten–Baumann method [2] has been shown by A. Robertson, R. Robinson, and Miss A. M. Struthers [3] to be 2-benzoyloxy-4 : 6-dihydroxybenzaldehyde (II), and has provided the means of attaining this object. On condensation with acetylated derivatives of substituted ω-hydroxyacetophenones by means of hydrogen chloride in ethyl acetate or ethyl acetate–alcohol, benzoylated anthocyanidins result, the acetyl groups being removed by hydrolysis either during the reaction or in the crystallisation of the product. Hydrolysis with aqueous-alcoholic sodium hydroxide and subsequent treatment with hydrochloric acid then yields the anthocyanidin with intermediate rupture of the pyrylium ring. Thus the use of ω : 3 : 4-triacetoxyacetophenone (III) leads first to 5-*O*-benzoylcyanidin chloride (IV) and then to cyanidin chloride [4] (V); by a similar process ω : 4-diacetoxyacetophenone gives ultimately pelargonidin chloride [5] (VI), and ω : 4-diacetoxy-3-methoxyacetophenone yields peonidin chloride [6] (VII). The colour reactions of the

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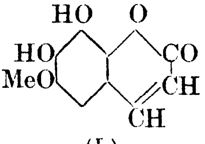
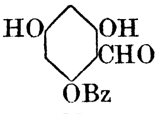
[49] From this point of view the 10-17-11-formula (11-ethyl) comes next in order of probability, and all the others seem out of the question.

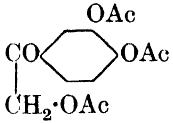
[1] *Ber.*, 1928, **61**, [*B*], 1279; **A.**, 893.



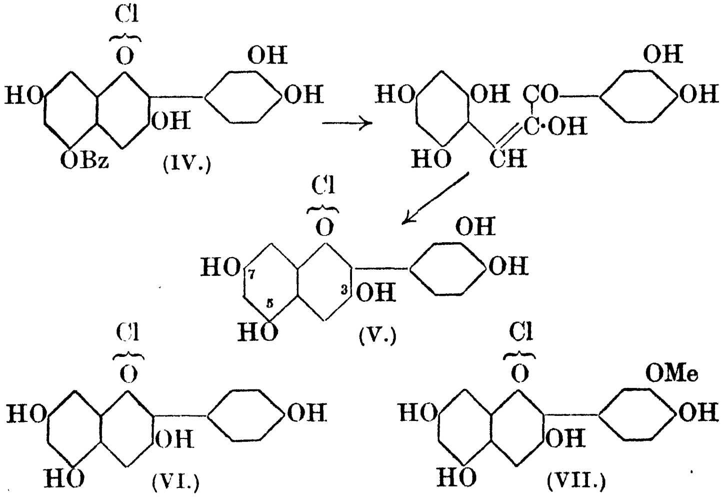
(I.)



(II.)



(III.)



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[2] A. Robertson and R. Robinson, *J.*, 1927, 1710.

[3] *J.*, 1928, 1455.

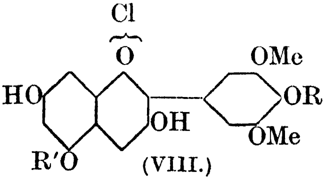
[4] A. Robertson and R. Robinson, *ibid.*, p. 1526.

[5] A. Robertson, R. Robinson, and J. Sugiura, *ibid.*, p. 1533.

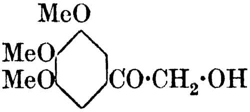
[6] S. Murakami and R. Robinson, *ibid.*, p. 1537.

synthetic cyanidin chloride were carefully compared with those of a specimen of natural origin, and left no doubt concerning the constitution of the latter. The view expressed by T. Malkin and M. Nierenstein [7] that cyanidin chloride is not 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride (V), since synthetical specimens of the latter show reactions which differ from those of the product from cyanin chloride, is believed by A. Robertson and R. Robinson not to be sound. These authors affirm that the older synthetical processes are not always trustworthy and are unsatisfactory for the production of cyanidin, and they do not regard the preparations of T. Malkin and M. Nierenstein as pure specimens of 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride.

Malvidin chloride (syringidin chloride), the diglucoside of which is malvin chloride, the anthocyanin of the violet flowers of the wild mallow (*Malva sylvestris*), has been regarded [8] as the dimethyl ether of delphinidin chloride with the structure (VIII; R = R′ = H). This anthocyanidin has now been prepared by W. Bradley and R. Robinson [9] by condensing *O*-benzoylphloroglucinaldehyde (II) with 3 : 4 : 5-trimethoxybenzoylcarbinol (IX) along lines similar to those described above, with the ultimate formation of delphinidin chloride 3′ : 4′ : 5′-trimethyl ether (VIII; R = Me; R′ = H), which was converted into malvidin chloride (VIII; R = R′ = H) by hydrogen bromide in acetic acid at 45—50°.



(VIII.)



(IX.)

Since, however, the final stage admits of demethylation in more than one way and still leaves doubt concerning the real structure of the product, these authors also developed the following synthesis. *O*-Benzoylphloroglucinaldehyde was made to condense with ω-acetoxy-4-benzyloxy-3 : 5-dimethoxyacetophenone (X) in ethyl acetate in the presence of hydrogen chloride to yield benzoylmalvidin chloride (VIII; R = H; R′ = Bz), hydrolysis of the benzyloxy- and acetoxy-groups taking place; subsequent debenzoylation yielded malvidin chloride, which proved to be identical with a specimen obtained from malvin chloride.

Investigations which have involved the application of the anthocyanidin syntheses of Pratt and Robinson to substances containing the glucose residue with the formation of glucosidoxyflavylium salts [10] have now led to the preparation of a naturally occurring anthocyanin. A. Robertson and R. Robinson [11] have succeeded in synthesising 3-β-glucosidylpelargonidin chloride (XI), which is undoubtedly identical with callistephin chloride, an anthocyanin isolated by R. Willstätter and C. L. Burdick [12] from the purple-red aster, thus providing the first synthesis of an actual flower pigment. ω-*O*-Tetra-acetyl-β-glucosidoxy-4-acetoxyacetophenone (XII) was obtained by the action of dry silver carbonate on a benzene solution of ω-hydroxy-4-acetoxyacetophenone and *O*-tetra-acetyl-α-glucosidyl bromide, and, when treated in a mixture of ether and chloroform with *O*-benzoylphloroglucinaldehyde (II) and dry hydrogen chloride, this yielded 3-*O*-tetra-acetyl-β-glucosidoxy-7-hydroxy-5-benzoyloxy-4′-acetoxyflavylium chloride (XIII). The anthocyanin, callistephin chloride (XI), was obtained from the latter by hydrolysis with cold 8% aqueous sodium hydroxide and subsequent acidification with hydrochloric acid, and, on further hydrolysis by heating with hydrochloric acid, it yielded pelargonidin chloride (VI).

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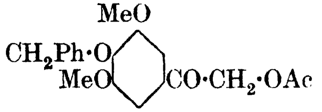
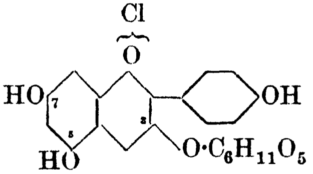
[7] *Ber.*, 1928, **61**, [*B*], 791; **A.**, 646.

[8] Miss E. S. Gatewood and R. Robinson, *J.*, 1926, 1959.

[9] *J.*, 1928, 1541.

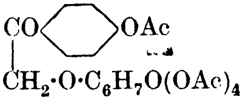
(X.)

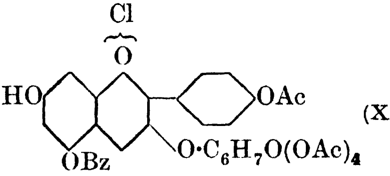




(XI.)

(XII.)





(XIII.)

The proof that callistephin is a 3-glucoside of pelargonidin has thrown light on the constitution of the isomeric anthocyanin, pelargonenin, and gives definite indications of the position of the saccharide residue in many anthocyanins. These authors, from a review of the evidence available, now suggest the 5-saccharide structure for pelargonenin, pelargonin, peonin, and cyanin. The fact that the various synthetic benzoylated anthocyanidins described above, which have the benzoyl group in the 5-position, exhibit the alkali colour reactions of the corresponding anthocyanins (cyanin, pelargonin, peonin, and malvin) confirms these views, although P. Karrer and his co-workers[13] have previously maintained that the saccharide residue is in the 3-position in these products.

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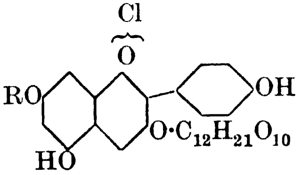
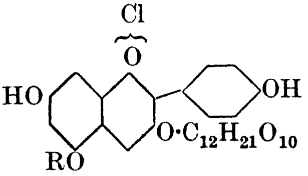
[10] A. Robertson and R. Robinson, *J.*, 1926, 1713; 1927, 242, 1710.

[11] *J.*, 1928, 1460.

[12] *Annalen*, 1916, **412**, 149.

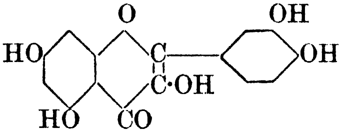
P. Karrer and R. Widmer[14] have considered the position of the acid residue which is present in some of the vegetable colouring matters. In particular, monardæin, extracted from the flowers of *Monarda didyma* with 2% methyl-alcoholic hydrochloric acid, can be hydrolysed by alkalis to the anthocyanin (monardin) and *p*-hydroxycinnamic acid. Methylation of monardæin in almost neutral solution gave a product which was insoluble in alkalis, but which could be hydrolysed by dilute methyl-alcoholic potassium hydroxide to *p*-methoxycinnamic acid and the dimethyl ether of monardin, which was soluble in an excess of alkali. The *p*-hydroxycinnamoyl group is thus not in the sugar residue, but replaces the hydrogen atom of a phenolic hydroxyl group in monardin, and other evidence indicates that it is in the phloroglucinol nucleus. Thus monardæin is represented by (XIV) or (XV). Further hydrolysis of monardin dimethyl ether with hydrochloric acid yielded the dimethyl ether of pelargonidin chloride (VI) and two molecules of dextrose. As a result of a similar investigation with delphinin, the anthocyanin from *Delphinium consolida*, it is apparent that the two molecules of *p*-hydroxybenzoic acid which are present are also attached to phenolic hydroxyl groups.[15]

(XIV.)




(XV.)

R = $HO\cdot C_6H_4\cdot CH{:}CH\cdot CO$.

(XVI.)


The main colouring matter of the red rose petals is the anthocyanin, cyanin, but the presence of a yellow pigment has been mentioned by G. Currey.[16] This has now been identified by P.

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[13] *Helv. Chim. Acta*, 1927, **10**, 729; **A.**, 1927, 1197.

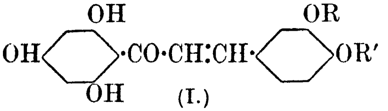
[14] *Ibid.*, 1928, **11**, 837.

[15] K. Kondo, *ibid.*, 1928, **11**, 919.

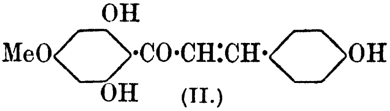
[16] *Proc. Roy. Soc.*, 1922, [*B*], **93**, 194; *A.*, 1922, i, 413.

Karrer and K. Schwarz[17] as a glucoside of quercetin (XVI), the flavonol corresponding to cyanidin chloride.

Flavanones, Flavones, and iso*Flavones.*—As a result of the work of F. Tutin[18] the structures assigned to eriodictyol (I; R = R′ = H) and homoeriodictyol (I; R = Me; R′ = H), from eriodictyon leaves, and to hesperitin (I; R = H; R′ = Me), the glucoside of which is hesperidin from the peel of orange, lemon, and related fruits, were considered to be definitely settled, the main evidence for a chalkone (phenyl styryl ketone) formula being derived from the fact that all these substances yield 2 : 4 : 6-trimethoxyphenyl 3 : 4-dimethoxystyryl ketone, identical with the product obtained from 2 : 4 : 6-trimethoxyacetophenone and vanillin methyl ether, on complete methylation. The related substance, naringenin, was considered to be 2 : 4 : 6-trihydroxyphenyl 4-hydroxystyryl ketone. More recently Y. Asahina, J. Shinoda, and M. Inubuse[19] have



(I.)



(II.)

examined the closely allied substance, sakuranetin, the glucoside of which is sakuranin from the bark of *Prunus yedoensis* and *P. serrulata.* Since its diacetyl derivative yields 2 : 4 : 6-trimethoxyphenyl 4-methoxystyryl ketone with methyl sulphate in hot alcoholic potassium hydroxide, and since complete hydrolysis of the glucoside gives *p*-hydroxybenzaldehyde and 2 : 6-dihydroxy-4-methoxyacetophenone, this product might appear to be 2 : 6-dihydroxy-4-methoxyphenyl 4-hydroxystyryl ketone (II). These authors, however, regard sakuranetin as being 5 : 4′-dihydroxy-7-methoxyflavanone (III; R = Me), with the glucose residue in the 5-position. It gives a diacetyl derivative, and, in pyridine, a monobenzoyl derivative. There is no colour with concentrated hydrochloric acid, whereas 2 : 4 : 6-trimethoxyphenyl 4-methoxystyryl ketone becomes deep reddish-brown. A purple-red colour is produced with magnesium and alcoholic hydrochloric acid, which is characteristic of hydroxy- and methoxy-flavanones but is not developed by derivatives of phenyl styryl ketone. Moreover, its absorption spectrum is practically identical with that of 5 : 7 : 4′-trimethoxyflavanone. The view is now put forward[20] that the related products, eriodictyol, homoeriodictyol, hesperitin, and naringenin, are really flavanone derivatives and that energetic methylation or acetylation produces derivatives of phenyl styryl ketone, the flavanone passing by

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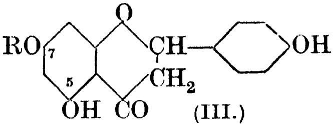
[17] *Helv. Chim. Acta*, 1928, **11**, 916.

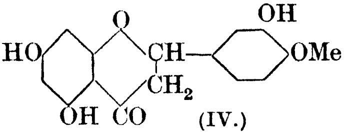
[18] *J.*, 1910, **97**, 2054.

[19] *J. Pharm. Soc. Japan*, 1927, 133; *Chem. Zentr.*, 1928, i, 1672.

[20] Y. Asahina, J. Shinoda, and M. Inubuse, *ibid.*, **48**, 29; *Chem. Zentr.*, 1928, ii, 49.



(III.)



(IV.)

isomeric change into the chalkone structure. Hesperitin, for example, is regarded as 5 : 7 : 3′-trihydroxy-4′-methoxyflavanone (IV). Naringenin, the glucoside of which is naringin from the blossoms of *Citrus decumana*, has been shown by Y. Asahina and M. Inubuse [21] to yield a triacetyl derivative with acetic anhydride and a drop of concentrated sulphuric acid. This gives no colour with ferric chloride, but a red colour with magnesium and hydrochloric acid. Prolonged heating with acetic anhydride and sodium acetate produces a tetra-acetyl derivative, which gives no such colour. Methylation with diazomethane gives naringenin dimethyl ether, which is identical with sakuranetin monomethyl ether. Naringenin is, therefore, considered to be 5 : 7 : 4′-trihydroxyflavanone (III; R = H).

J. Shinoda and S. Sato [22] have found that, although polyhydric phenols in general condense with cinnamoyl chloride in nitrobenzene in the presence of aluminium chloride to give chalkones, the use of phloroglucinol leads to the isomeric flavanones, and have employed this reaction for preparing some of these naturally occurring products. From phloroglucinol and *O*-carbethoxy-*p*-hydroxycinnamoyl chloride, naringenin has been obtained,[23] and the use of *O*-carbethoxy-3-hydroxy-4-methoxycinnamoyl chloride leads to hesperitin.[24]

The reduction of hydroxyflavonols with magnesium and hydrochloric acid has been known to yield anthocyanidins (quercetin, *e.g.*, gives cyanidin chloride). Y. Asahina and M. Inubuse [25] have now found that benzopyrylium salts also result from the reduction of hydroxyflavones with sodium amalgam and subsequent addition of hydrochloric acid, and also from hydroxy- and methoxy-flavanones, either with magnesium and hydrochloric acid or with sodium amalgam and subsequent addition of hydrochloric acid. Thus apigeninidin chloride (VII) results from both apigenin (V) and naringenin (III; R = H). The reduction of apigenin is believed to proceed in the following stages :

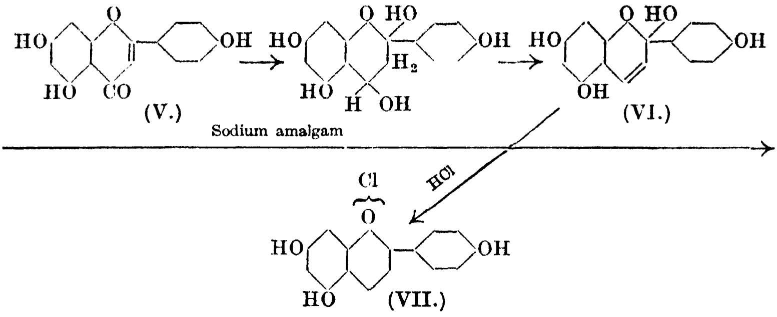
[21] *Ber.*, 1928, **61**, [*B*], 1514; **A.**, 1020.

[22] *J. Pharm. Soc. Japan*, **48**, 109; *Chem. Zentr.*, 1928, ii, 1885.

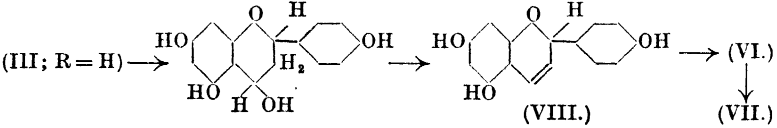
[23] J. Shinoda and S. Sato, *ibid.*, **48**, 117.

[24] J. Shinoda and M. Kawagoye, *ibid.*, **48**, 119.

[25] *Ber.*, 1928, **61**, [*B*], 1646.



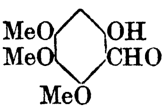
and for the reduction of naringenin the following mechanism is suggested :

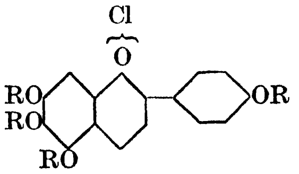


It is assumed that the change (VIII) ⟶ (VI) proceeds through the agency of atmospheric oxygen. Observations of this kind are of interest in showing the relationships between these various classes of naturally occurring products.

E. Chapman, A. G. Perkin, and R. Robinson [26] have described the isolation of two red colouring matters, carajurin and carajurone, from carajura.[27] Demethylation of carajurin, $C_{17}H_{14}O_5$, by boiling with hydriodic acid, yields carajuretin hydriodide, $C_{15}H_{11}O_5I$, which behaves like a tetrahydroxyflavylium iodide and yields carajuretin, $C_{15}H_{10}O_5$, with cold pyridine : fission of carajurin with boiling concentrated aqueous potassium hydroxide gives *p*-acetylanisole. The absence of any tendency in these substances to pass into pseudo-bases indicates the relationship to the flavone rather than the flavonol type. The action of hydrogen chloride on a mixture of antiarolaldehyde (IX) and *p*-acetylanisole in acetic acid led to the formation of 5 : 6 : 7 : 4′-tetramethoxyflavylium chloride (X; R = Me), which gave scutellareinidin iodide on

(IX.)





(X.)

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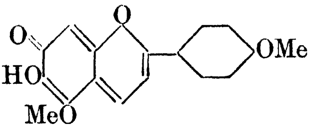
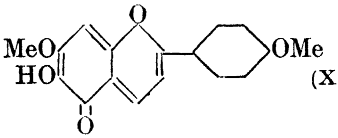
[26] *J.*, 1927, 3015.

[27] A. G. Perkin (*P.*, 1914, **30**, 212) mentions the separation of carajurin and carajurone from carajura.

demethylation with hydriodic acid. The corresponding chloride (X; R = H), obtained from it by the action of silver chloride, is identical with carajuretin hydrochloride. Carajurin itself, therefore, possesses one of the formulæ (XI) and (XII), of which (XI) is considered to be the more probable. Carajurone is probably a carajuretin monomethyl ether, $C_{16}H_{12}O_5$.

(XI.)

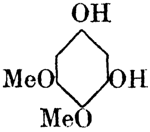


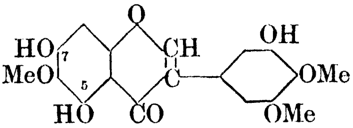


(XII.)

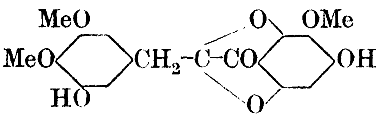
Irigenin, obtained by the hydrolysis of the glucoside iridin contained in the dried rhizomes of the *Iris florentina*, has now been shown by W. Baker[28] to be a member of the comparatively rare *iso*flavone (3-phenylchromone) group of naturally occurring products with the formula (XIV) (5 : 7 : 3′-trihydroxy-6 : 4′ : 5′-trimethoxy*iso*flavone). Previously G. de Laire and F. Tiemann[29] had assigned the formula (XV) to this product, and G. Bargellini[30] had regarded it as a coumarin derivative (XVI). Thus it gives a

(XIII.)

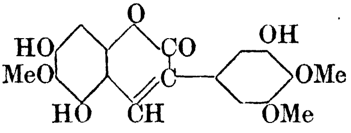




(XIV.)



(XV.)



(XVI.)

dibenzoyl derivative which gives a ferric chloride reaction (the 5-OH group, being ortho to the carbonyl group, has very weak phenolic properties, but gives a ferric chloride reaction), a triacetyl derivative which can easily be hydrolysed to a diacetyl derivative, and a trimethyl ether which, on heating with potash, yields 3 : 4 : 5-trimethoxyphenylacetic acid and 3 : 4 : 5-trimethoxyphenol (antiarol). The hexahydric phenol, irigenol, from the demethylation of irigenin, gives an oxonium sulphate, $C_{15}H_{10}O_8,H_2SO_4$, the possibility of a coumarin structure thus being eliminated. Irigenin dimethyl ether with hot aqueous alkali in hydrogen yields 3 : 4 : 5-trimethoxyphenylacetic acid and 4 : 5-dimethoxyresorcinol (XIII). De Laire and Tiemann had previously obtained iridic acid (3-hydroxy-

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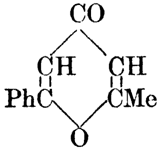
[28] *J.*, 1928, 1022. [29] *Ber.*, 1893, **26**, 2010. [30] *Gazzetta*, 1925, **55**, 945.

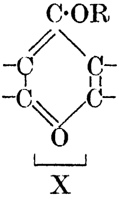
4 : 5-dimethoxyphenylacetic acid), iretol (methoxyphloroglucinol), and formic acid from irigenin by treatment with aqueous potassium hydroxide in an atmosphere of hydrogen. In iridin, the glucose residue has been shown by W. Baker to be attached to the 7-position.

An account by F. A. Mason[31] of the recent extensive investigations of K. Freudenberg and his collaborators, which have resulted in the elucidation of the structures of catechin and *epi*catechin and have established the relationship between these substances and cyanidin, has appeared during the year.

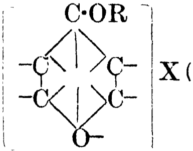
Turning to other work on oxygen ring compounds, C. S. Gibson and J. L. Simonsen[32] have been unable to separate the *d*-α-bromocamphor-π-sulphonate of 2-phenyl-6-methyl-4-pyrone (I) into diastereoisomerides, and regard this as support, although based on negative results, for the more usually accepted structures[33] (II) and (III) for the salts of γ-pyrones, since the oxonium[34] (IV) and bridge[35] (V) formulations would indicate the possibility of resolving appropriate salts derived from unsymmetrical γ-pyrones.

(I.)



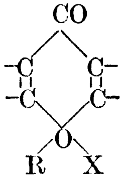


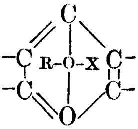
(II.)



(III.)

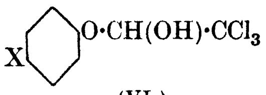
(IV.)



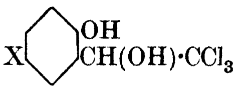


(V.)

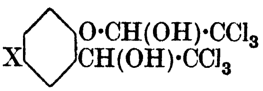
F. D. Chattaway and his collaborators[36] have recently investigated an interesting reaction between para-substituted phenols and chloral hydrate in the presence of concentrated sulphuric acid, whereby derivatives of 2 : 4-bistrichloromethyl-1 : 3-benzdioxin (IX; X = NO_2, CO_2H, SO_3H, NH_2, etc.) are formed, probably



(VI.)



(VII.)



(VIII.)

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[31] *J. Soc. Chem. Ind.*, 1928, **47**, 269T.

[32] *J.*, 1928, 2307.

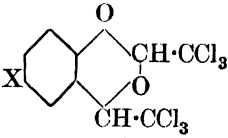
[33] A. Baeyer, *Ber.*, 1910, **43**, 2337; A. Werner, *Ber.*, 1901, **34**, 3309; A. Hantzsch, *Ber.*, 1919, **52**, 1535, 1544.

[34] J. N. Collie and T. Tickle, *J.*, 1899, **75**, 710.

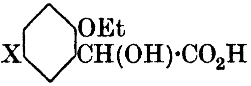
[35] J. N. Collie, *J.*, 1904, **85**, 971.

[36] *J.*, 1926, 2720; 1927, 685, 2013; 1928, 1088, 2913, 3241.

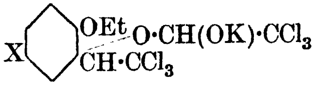
through the intermediate stages (VI), (VII), and (VIII). With alcoholic potash these 1 : 3-benzdioxins give the corresponding



(IX.)

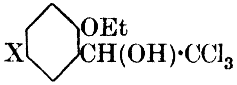


(X.)

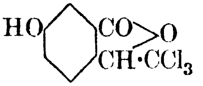


(XI.)

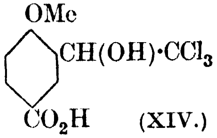
5-substituted derivatives of 2-ethoxyphenylglycollic acid (X), probably through the intermediate stages (XI) and (XII), a reaction which indicates the constitution of (IX). If the *p*-position in the phenol is unoccupied, the $-CH(OH)\cdot CCl_3$ group may enter there, as is indicated by the formation of 5-hydroxytrichloromethylphthalide (XIII) from *m*-hydroxybenzoic acid. When chloral



(XII.)



(XIII.)



(XIV.)

hydrate is allowed to react with the corresponding alkyl ethers, these 1 : 3-benzdioxins cannot be produced, but a single $-CH(OH)\cdot CCl_3$ group replaces a hydrogen atom ortho to the alkoxyl group. Thus *p*-anisic acid and chloral hydrate react together in concentrated sulphuric acid to give 5-carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene (XIV).

The formation of benzdioxins also takes place when dichloroacetaldehyde alcoholate is used in the place of chloral hydrate. For instance, with *p*-nitrophenol the product is 6-nitro-2 : 4-bisdichloromethyl-1 : 3-benzdioxin, and this also is converted ultimately into 5-nitro-2-ethoxyphenylglycollic acid by alcoholic potash, a reaction which, in this case, involves oxidation. It is apparent, therefore, that this condensation, which leads to a benzdioxin, is a feature of those aldehydes which are comparatively stable in concentrated sulphuric acid.

Pyrrole Derivatives.

Many of the papers on pyrrole derivatives which have appeared during the year have been concerned with further developments in the chemistry of the porphyrins.

W. H. Gray[37] has shown that the product obtained by heating *d*-glutamic acid with aniline is *l*-2-pyrrolidone-5-carboxyanilide (I). It had previously been regarded as 2-hydroxypyrroline-5-carboxylic acid (II), the enolic form of 2-pyrrolidone-5-carboxylic acid, by

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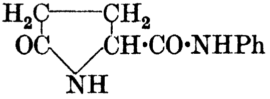
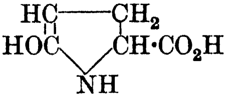
[37] *J.*, 1928, 1264.

E. Abderhalden and E. Schwab,[38] who believed that the same substance was also produced by the action of diphenylamine on *d*-glutamic acid.[39] W. H. Gray, however, has found that the products

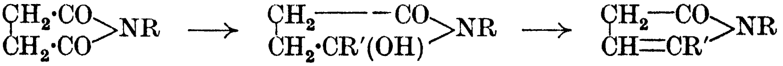
(I.)





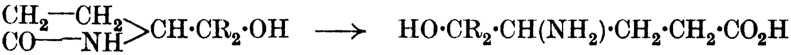
(II.)

of the latter reaction are *l*- and *dl*-2-pyrrolidone-5-carboxylic acid. Several substituted pyrrolones have been prepared, through the intermediate hydroxypyrrolidone, by the action of Grignard reagents on *N*-substituted succinimides.[40]



$$\left.\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}\right>NR \longrightarrow \left.\begin{matrix}CH_2\text{———}CO\\CH_2\cdot CR'(OH)\end{matrix}\right>NR \longrightarrow \left.\begin{matrix}CH_2\text{—}CO\\CH{=}CR'\end{matrix}\right>NR$$

Ethyl *p*-aminobenzoate, pyruvic acid, and benzaldehyde react together in alcoholic solution to yield, first, 4 : 5-diketo-2-phenyl-1-*p*-carbethoxyphenylpyrrolidine, and then, through further condensation with ethyl *p*-aminobenzoate, 4-*p*-carbethoxyphenylimino-5-keto-2-phenyl-1-*p*-carbethoxyphenylpyrrolidine.[41] Other aromatic aldehydes can be used in the place of benzaldehyde in these reactions. δ-Bromo-α-dimethylaminobutan-γ-one hydrobromide passes, on treatment with aqueous barium hydroxide, into 3-keto-1 : 1-dimethylpyrrolidinium bromide. The corresponding chloride, on catalytic hydrogenation, gives 3-hydroxy-1 : 1-dimethylpyrrolidinium chloride, which yields 3-hydroxy-1-methylpyrrolidine on thermal decomposition in an atmosphere of nitrogen.[42] α-(2-Pyrrolidonyl)-dialkylcarbinols (III), which can be obtained by the action of Grignard reagents on ethyl glutamate, are easily hydrolysed by alkalis to give the γ-amino-δ-hydroxy-δδ-dialkylvaleric acids.[43]



$$\left.\begin{matrix}CH_2\text{—}CH_2\\CO\text{——}NH\end{matrix}\right>CH\cdot CR_2\cdot OH \longrightarrow HO\cdot CR_2\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO_2H$$

(III.)

Mention might be made in this section of the isolation of selenophen, the selenium analogue of thiophen and apparently hitherto unknown, by H. V. A. Briscoe and J. B. Peel [44] from the product of the action of acetylene on selenium at 400°. These authors regard as untrustworthy the statement made by I. Foa[45] that selenophen results from heating sodium succinate with phosphorus triselenide. Selenophen is a liquid (b. p. 109·9—110·1°/752·1 mm.; f. p. − 38°) which chemically resembles thiophen in stability and inactivity, and gives an indophenin reaction with isatin and concentrated sulphuric acid. In carbon disulphide, with bromine it yields tetrabromoselenophen and with chlorine tetrachloroselenophen.

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[38] *Z. physiol. Chem.*, 1926, **153**, 88; **A.**, 1926, 734.

[39] *Ibid.*, 1926, **157**, 196.

[40] R. Lukeš, *Chem. Listy*, 1928, **22**, 1; **A.**, 299; R. Lukeš and V. Prelog, *ibid.*, p. 244; **A.**, 897.

[41] S. Weil and S. Auerbachówna, *Rocz. Chem.*, 1927, **7**, 357; **A.**, 1928, 70; S. Weil and (Mlle.) F. Goldberg, *ibid.*, p. 585; **A.**, 527.

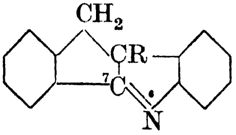
[42] C. Mannich and T. Gollasch, *Ber.*, 1928, **61**, [*B*], 263; **A.**, 427.

[43] S. Kanao and S. Inagawa, *J. Pharm. Soc. Japan*, 1928, No. 554, 355; **A.**, 1022.

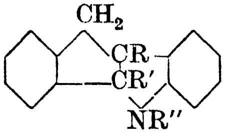
[44] *J.*, 1928, 1741.

Indole Derivatives.

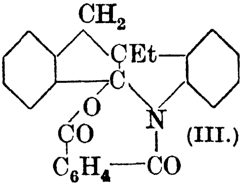
H. Leuchs and his co-workers[46] have observed some interesting reactions in the indolenine series with the indeno-ψ-indolines (I; R = Et, Ph, or CH_2Ph). For instance, acetic anhydride and sodium acetate at 100° gave the 7-acetoxy-6-acetyl addition product (II; R′ = OAc; R″ = Ac), benzoic anhydride the corresponding 7-benzoyloxy-6-benzoyl derivative (II; R′ = OBz; R″ = Bz),



(I.)



(II.)



(III.)

and phthalic anhydride at 160° the product (III). Methyl-alcoholic ammonia caused the 6 : 7 addition of H and NH_2 (II; R′ = NH_2; R″ = H), and the addition of hydrogen was effected by zinc amalgam and hydrochloric acid. These 7-acetoxy- and 7-benzoyloxy-compounds were converted into the corresponding 7-methoxy-derivatives by boiling with methyl alcohol, into the 7-hydroxy-compounds by hydrochloric acid in acetic acid, and into the 7-amino-compounds by methyl-alcoholic ammonia.

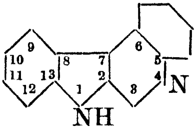
Two methods for synthesising derivatives of 5 : 6-benz-4-carboline (IV), described by W. O. Kermack and R. H. Slater,[47] are of interest in alkaloid chemistry. 3-*o*-Nitrophenylindole-2-carboxylic acid (V), prepared from *o*-nitrophenylpyruvic acid phenylhydrazone by Fischer's method, was reduced by zinc dust in acetic acid solution, ring closure taking place at the same time, to give 3-keto-3 : 4-dihydro-5 : 6-benz-4-carboline (VI). The latter substance was reduced by zinc dust in an atmosphere of hydrogen to 5 : 6-benz-4-carboline (IV). An alternative method is to convert 3-*o*-nitrophenylindole-2-carboxylic acid (V) into 3-*o*-nitrophenylindole by heating its

[45] *Gazzetta*, 1909, **39**, ii, 527.

[46] *Annalen*, 1928, **461**, 27; **A.**, 528.

[47] *J.*, 1928, 32.

ammonium salt, to reduce this to 3-*o*-aminophenylindole with iron and hydrochloric acid in alcoholic solution, and then to treat its formyl derivative with phosphorus oxychloride in boiling toluene. Homologues of 5 : 6-benz-4-carboline were obtained in a similar way, by using other acyl derivatives of 3-*o*-aminophenylindole, or by starting with *o*-nitrophenylpyruvic acid phenylmethylhydrazone.



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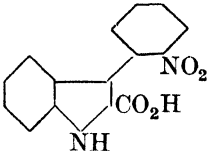

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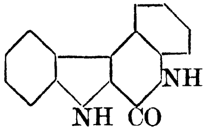
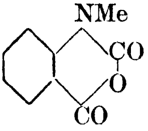


(VI.)

W. O. Kermack and R. H. Slater [48] have confirmed, by investigations with 5 : 6-benz-4-carboline derivatives, the views held concerning anhydronium base formation in the carboline series and the course of the addition of alkyl salts to these bases.[49] Thus the action of alkalis on 5 : 6-benz-4-carboline methosulphate gave an anhydronium base, the methosulphate of which was shown to be identical with 1-methyl-5 : 6-benz-4-carboline methosulphate.

Following on the synthesis of rutæcarpine,[50] Y. Asahina and T. Ohta [51] have now synthesised evodiamine, the other alkaloid from *Evodia rutæcarpa*. *N*-Methylisatoic anhydride (VII), obtained by heating *N*-methylanthranilic acid and ethyl chloroformate, was converted by warming with 3-β-aminoethylindole into 3-β-*o*-methylaminobenzoylaminoethylindole (VIII), which, on heating for 18 hours at 175—180° with ethyl orthoformate, yielded *r*-evodiamine (IX). Y. Asahina and T. Ohta [52] have also developed further



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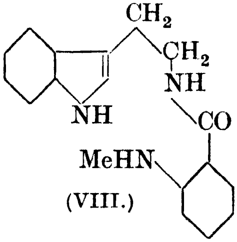

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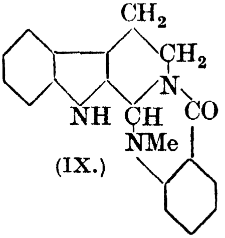

(IX.)

syntheses of rutæcarpine (X). They have obtained 3-β-aminoethylindole-2-carboxylic acid by the action of alcoholic potassium hydroxide on 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (XI). Since they had previously prepared rutæcarpine from the *N*-*o*-nitrobenzoyl derivative of this acid by reduction and subsequent dehydration,[53] the synthesis is complete. Alternatively, the *N*-*o*-nitrobenzoyl derivative of 3-β-aminoethylindole-2-carboxylic acid was found to yield *N*-*o*-nitrobenzoyl-3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline with phosphorus oxychloride in carbon tetrachloride, and this, on reduction with zinc dust and glacial acetic acid, gave rutæcarpine.

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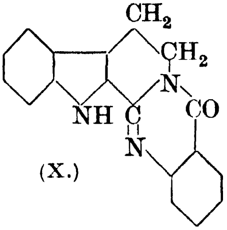
[48] *J.*, 1928, 789.

[49] Compare W. H. Perkin and R. Robinson, *J.*, 1919, **115**, 942.

[50] Y. Asahina, R. H. F. Manske, and R. Robinson, *J.*, 1927, 1708; *Ann. Reports*, 1927, **24**, 161.

[51] *Ber.*, 1928, **61**, [*B*], 319; **A.**, 432.

[52] *J. Pharm. Soc. Japan*, **48**, 51; *Chem. Zentr.*, 1928, ii, 58.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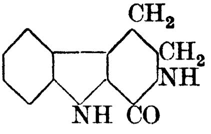
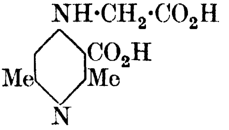

(XI.)

E. Koenigs and H. Kantrowitz,[54] by the action of acetic anhydride on 3-carboxy-2 : 6-dimethyl-4-pyridylaminoacetic acid (XII), have prepared 4 : 6-dimethylpyrindoxyl (XIII), but attempts to oxidise this to the corresponding pyrindigotin failed. The action of acetic anhydride on 3-carboxy-2 : 6-dimethylpyridyl-4-thiolacetic acid (XIV) yielded 3-hydroxy-4 : 6-dimethylpyridothiophen (XV), oxidation of which in alkaline solution at 70° in the presence of spongy platinum gave 4 : 6 : 4′ : 6′-tetramethylthiopyrindigotin (XVI) : (XIV) could also be converted directly into (XVI) by the action of concentrated sulphuric acid at 210—215°. The latter process is similar to that used by E. Plazek and E. Sucharda [55] for converting 2-carboxypyridine-3-thiolacetic acid (XVII) into the corresponding δ-thiopyrindigotin (XVIII). The analogous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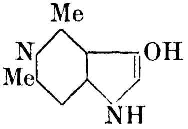
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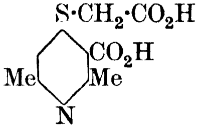
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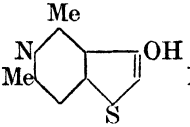
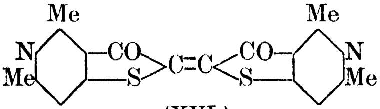

(XV.)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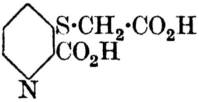
(XVII.)

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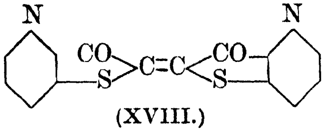
[53] *J. Pharm. Soc. Japan*, 1927, No. 543, 51; *Chem. Zentr.*, 1927, ii, 940.

[54] *Ber.*, 1927, **60**, [*B*], 2097; **A.**, 1927, 1207.

[55] *Ber.*, 1926, **59**, [*B*], 2282; **A.**, 1926, 1263.

δ-pyrindigotin (XIX) was prepared by E. Sucharda [56] from 3-pyridylglycine-2-carboxylic acid by fusion with potassium hydroxide and subsequent atmospheric oxidation. These indigotin derivatives gave the corresponding leuco-compounds by various methods, but the processes were more difficult than in the simple indigo and thioindigo series. They could, in general, be used as vat, and sometimes as basic, dyes.



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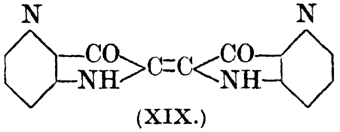

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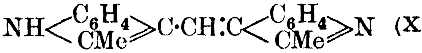

$$\mathrm{NH}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CMe}\end{matrix}>\mathrm{C{\cdot}CH{:}C}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CMe}\end{matrix}>\mathrm{N}$$ (XX.)

The view that complex, additive, metallic compounds of copper, zinc, etc., with indigotin and with 2-methylindolyl-2-methylindolidenemethane (XX) can be formed without replacement of hydrogen [57] is held to be unsound. It has been shown [58] that the formation of these products involves replacement of hydrogen, and they are now represented as co-ordinated derivatives of a more conventional type.

Pyridine Derivatives.

Pyridine is rapidly oxidised, by warming at 70° with aqueous potassium permanganate and sulphuric acid, to carbon dioxide and ammonia, small amounts of nitric acid being also formed.[59] Oxidation with sodium persulphate produces a similar result,[60] and prolonged boiling of pyridine with aqueous potassium permanganate alone leads to ammonium carbonate and the potassium salts of carbonic, oxalic, nitric, and nitrous acids.[61] Homologues of pyridine are oxidised in a similar way, and the instability of the nucleus accounts for the low yields of pyridinecarboxylic acids obtained under these conditions.

It has been found by E. Späth and G. Burger [62] that benzoylacetaldehyde condenses with ethyl aminocrotonate in ether to yield ethyl 6-phenyl-2-methylpyridine-3-carboxylate with none of the isomeric ethyl 4-phenyl-2-methylpyridine-3-carboxylate. A. E. Tschitschibabin and his co-workers[63] have investigated many of the simpler derivatives of pyridine. 3-Nitroaminopyridine was prepared from 3-aminopyridine by the action of nitric acid (*d* 1·5) in concentrated sulphuric acid solution, and, unlike the corresponding 2- and 4-nitroamino-derivatives, which yield mainly aminonitropyridines on treatment with acids, it lost nitrous oxide under similar conditions and gave 3-hydroxypyridine. The 2-nitroamino-derivative does, however, give a small amount of 2-pyridone with concentrated sulphuric acid, and a 60% yield of this product with acetic acid. With methyl sulphate in alkaline solution, 3-nitroaminopyridine gave a salt which is believed to have the structure (I); the formula (II) is assigned to the substance obtained

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[56] *Ber.*, 1925, **58**, [*B*], 1724; *A.*, 1925, i, 1331.

[57] K. Kunz and co-workers, *A.*, 1923, i, 155, 1134; 1925, i, 1318; 1927, 366.

[58] R. Kuhn and H. Machemer, *Ber.*, 1928, **61**, [*B*], 118; **A.**, 306; O. Schmitz-Dumont and E. Motzkus, *ibid.*, p. 580; **A.**, 529.

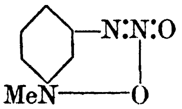
[59] M. Delépine, *Compt. rend.*, 1927, **184**, 206; **A.**, 1927, 254.

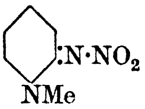
[60] J. Dorronsoro, *Anal. Fis. Quim.*, 1927, **25**, 409; **A.**, 185.

[61] B. D. Shaw and A. L. Wilkie, *J.*, 1928, 1377.

[62] *Monatsh.*, 1928, **49**, 265; **A.**, 1024.

(I.)





(II.)

from 2-nitroaminopyridine under similar conditions. 1-Methyl-2-pyridonenitroimide (II), with cold concentrated sulphuric acid, gave a mixture of 5-nitro- and 3-nitro-2-methylaminopyridine. 2-Dimethylaminopyridine differs from dimethylaniline in being unable to yield a nitroso-derivative or to couple with diazonium salts, but it can be directly nitrated to give the 5-nitro- and 3 : 5-dinitro-2-dimethylaminopyridines, and bromination in dilute sulphuric acid yields the corresponding mono- and di-bromo-derivatives. Although 2-aminopyridine can readily be converted into 3-nitro- and 5-nitro-2-aminopyridine through the intermediate formation of the 2-nitroamino-compound, direct nitration of 2-acetamidopyridine cannot be effected.[64] Nitric acid (*d* 1·5) in glacial acetic acid and acetic anhydride gives the nitrate, which is unaltered by boiling fuming nitric acid or a boiling mixture of nitric acid and acetic anhydride. The nitrate gives 3-nitro- and 5-nitro-2-aminopyridine with concentrated sulphuric acid, but nitration is preceded by hydrolysis of the acetamido-group. Direct bromination of 2-acetamidopyridine to the 5-bromo-derivative has, however, been carried out.

Quinoline Derivatives.

Cyanine Dyes.—The investigations amongst the many classes of cyanine dyes have been extended in several directions during the year. W. H. Mills and H. G. Ordish [65] have established the constitution of the *apo*cyanines, proving the structure suggested by A. Kaufmann and P. Strübin [66] to be incorrect. The action of alcoholic potassium hydroxide on a quinoline alkyliodide alone gives a mixture of two isomeric dyes, $(C_{18}H_{13}N_2R_2)I$, a xantho*apo*cyanine (yellow) and an erythro*apo*cyanine (red). Oxidation of the erythro*apo*cyanine from quinoline ethiodide with iodine removes a hydrogen atom and inserts an iodine atom to give the diethiodide of a diquinolyl, $C_{18}H_{12}N_2$, which can itself be obtained by heating the corresponding diethochloride in a vacuum. The close resemblance between ethylerythro*apo*cyanine and the other classes of cyanine dye suggests the presence of two NEt groups (one in the ammonium form, and the other tervalent) connected by a chain of conjugated linkages which must have an odd number of carbon atoms. This diethiodide must therefore be derived from either 3 : 4′-diquinolyl (I ; R = H) or 3 : 2′-diquinolyl (II). The dyes will be derived from the corresponding diethiodides by removal of

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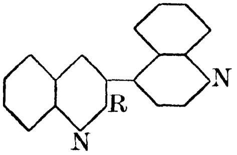
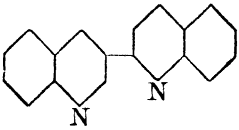
[63] *Ber.*, 1925, **58**, [*B*], 406; *A.*, 1925, i, 437; *ibid.*, 1927, **60**, [*B*], 2433; **A.**, 1928, 185; *ibid.*, 1928, **61**, [*B*], 427, 1223; **A.**, 427, 899.

[64] E. Plažek and E. Sucharda, *ibid.*, p. 1813; **A.**, 1260.

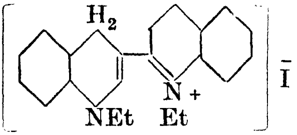
(I.)





(II.)

an iodine atom and insertion of a hydrogen atom, which must go into the 4-position in order to maintain the conjugated system. Thus the xantho*apo*cyanine can be represented by the tautomeric formulæ (III) and (IV), with a conjugated chain of three carbon atoms, and the more deeply coloured erythro*apo*cyanine by the tautomeric formulæ (V) and (VI), which have a conjugated chain of five carbon atoms. Similar formulæ have been suggested



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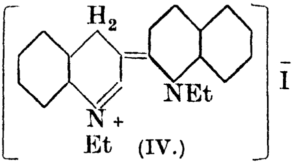

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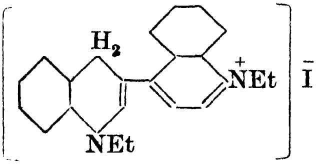

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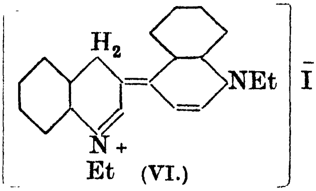


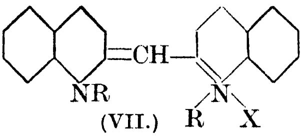
(VI.)

[65] *J.*, 1928, 81.

[66] *Ber.*, 1911, **44**, 690.

previously by W. König[67] without proof. The correctness of formula (V) or (VI) for the erythro*apo*cyanine has been established by Mills and Ordish by synthesising 3 : 4′-diquinolyl (I; R = H), and showing that its diethiodide is identical with that obtained by oxidising the dye with iodine. The synthesis was effected by condensing *o*-aminobenzaldehyde with ethyl 4-quinolylpyruvate to give ethyl 3 : 4′-diquinolyl-2-carboxylate (I; R = CO_2Et), from which the carbethoxy-group was subsequently eliminated.

Miss F. M. Hamer[68] has investigated the formation of the *ψ*-cyanine dyes (VII) by the action of alcoholic potassium hydroxide on a mixture of 2-iodoquinoline alkyliodide and quinaldine alkyliodide. Hitherto only two of these have been prepared,[69] and Miss Hamer has now prepared seven new ones, some of which are of value as photographic sensitisers, the action being in the bluish-green portion of the spectrum. The *ψ*-cyanine reaction can yield an *iso*cyanine (VIII), lepidine alkyliodide and 2-iodoquinoline alkyliodide being used.



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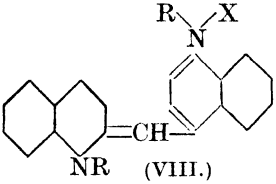

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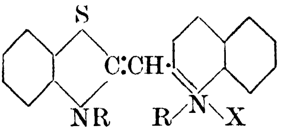

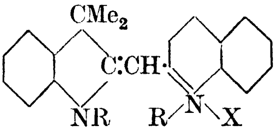

(X.)

A similar process with 1-methylbenzthiazole alkyliodide and 2-iodoquinoline alkyliodide leads to the thio-*ψ*-cyanines (IX), and in this way the structure assigned by W. H. Mills and W. T. K. Braunholtz[70] to one of the dyes obtained by heating quinaldine ethonitrate with di-*o*-formylethylaminodiphenyl disulphide in pyridine solution is confirmed. The *ψ*-cyanine reaction has been still further extended to the preparation of a new type of dye, the indo-*ψ*-cyanines (X), a substituted indolenine quaternary salt containing a reactive 2-methyl group and 2-iodoquinoline alkyliodide being used.

Miss F. M. Hamer[71] has also investigated three dyes of the neocyanine type, neocyanine ethiodide, ethobromide, and methobromide. These are obtained, together with the corresponding kryptocyanines (4 : 4′-carbocyanines), by the action of pyridine and ethyl orthoformate on lepidine alkyl salts,[72] and can be separated on account of their smaller solubility in spirit. Analyses indicate that the neocyanines are probably formed from three molecules of lepidine alkyl salt by condensation through their reactive methyl groups with one molecule of ethyl orthoformate, one molecule of hydrogen halide and two atoms of hydrogen being also eliminated. The structure (XI), derived in this way, represents the neocyanines as closely related to the kryptocyanines (XII) and accounts for the sensitising properties of these dyes, but it is not yet definitely established.

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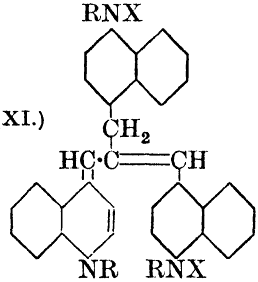
[67] *Ber.*, 1922, **55**, [*B*], 3293.

[68] *J.*, 1928, 206.

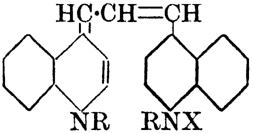
[69] O. Fischer, *J. pr. Chem.*, 1918, **98**, 204; O. Fischer and G. Scheibe, *ibid.*, 1919, **100**, 86.

[70] *J.*, 1923, **123**, 2804.

[71] *J.*, 1928, 1472.



(XI.)



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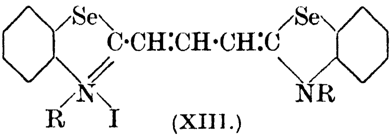

(XIII.)

By extending the reaction of Miss F. M. Hamer [73] for preparing the various classes of carbocyanines, L. M. Clark [74] has isolated two selenocarbocyanines, which are exactly analogous to the thiocarbocyanines. From 1-methylbenzselenazole methiodide and ethiodide respectively, with ethyl orthoformate and pyridine, 2 : 2′-dimethyl- and 2 : 2′-diethyl-selenocarbocyanine iodides (XIII) have been obtained : like their sulphur analogues, they sensitise the photographic plate. W. König [75] has prepared a number of substituted thiocarbocyanines, and has examined the effect of the substituents upon the colour of the dye.

Of considerable interest is the preparation by K. Fuchs and E. Grauaug [76] of dyes which differ from the carbocyanines in having the $=$CH–CH$=$CH– group replaced by $=$CH–N$=$N–. Thus a process which ultimately involves the condensation of 1-methyl-2-quinolonehydrazone (XIV) and quinoline-2-aldehyde methoperchlorate yielded the 1-methyl-2-quinolenylhydrazone of quinoline-2-aldehyde methoperchlorate (XV), which in its tautomeric form becomes (XVI); and 2-ethylbenzthiazolonehydrazone

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[72] Miss F. M. Hamer, *J.*, 1927, 2796; *Ann. Reports*, 1927, **24**, 165.

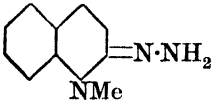
[73] *J.*, 1927, 2796; *Ann. Reports*, 1927, **24**, 166.

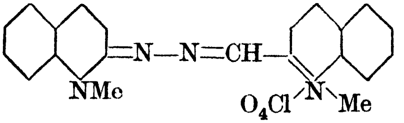
[74] *J.*, 1928, 2313.

[75] *Ber.*, 1928, **61**, [*B*], 2065.

[76] *Ibid.*, p. 57; **A.**, 430.

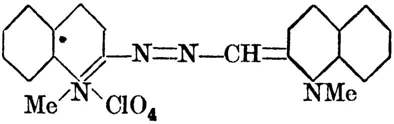
(XIV.)



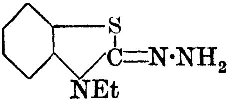


(XV.)

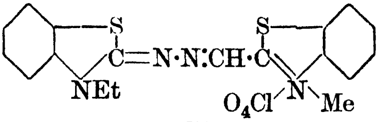
(XVI.)



(XVII) and benzthiazole-1-aldehyde methoperchlorate gave the 2-ethylbenzthiazolenylhydrazone of benzthiazole-1-aldehyde methoperchlorate (XVIII). By analogous reactions, similar dyes, containing both a quinoline and a benzthiazole nucleus, can be isolated. These dyes are strong desensitisers towards the photographic plate.

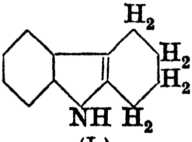


(XVII.)

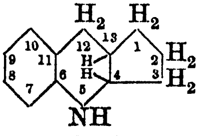


(XVIII.)

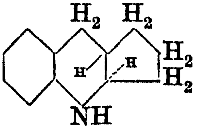
Reduced Quinolines.—The formation of two stereoisomerides, due to the *cis*- and *trans*-unions of two saturated ring systems, during the reduction of some heterocyclic compounds has been further investigated. The reduction of tetrahydrocarbazole (I) with tin and hydrochloric acid in aqueous alcohol leads to the *cis*-form of hexahydrocarbazole with only a very small amount of the *trans*-modification,[77] but it has now been observed by W. H. Perkin and S. G. P. Plant [78] that the reduction of 2 : 3-dihydroquinindene under similar conditions yields relatively considerable quantities of both the *cis*- and the *trans*-form of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (II and III). These results are interesting in view of the fact that a consideration of the multiplanar configurations concerned indicates that, whereas the *trans*-modification of



(I.)



(II.) *cis*-



(III.) *trans*-

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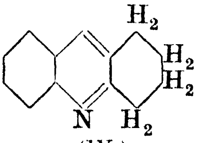
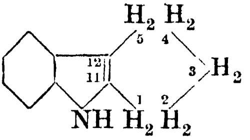
[77] J. Gurney, W. H. Perkin, and S. G. P. Plant, *J.*, 1927, 2676; *Ann. Reports*, 1927, **24**, 98.

[78] *J.*, 1928, 639.

hexahydrocarbazole is much more highly strained than the *cis*-, the two forms of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene are strained to approximately the same extent. Using similar experimental conditions, W. H. Perkin and S. G. P. Plant [79] have found that the reduction of tetrahydroacridine (IV) to octahydroacridine yields relatively considerable amounts of both forms,[80] but the hydrogenation of 2 : 3 : 4 : 5-tetrahydroheptindole (V) to 2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole, and of 7 : 8 : 9 : 10-tetrahydroheptaquinoline (VI) to 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline leads essentially to a single product in each case. The failure to isolate more than one of the two possible stereoisomerides when a 7-membered ring is concerned was surprising, since considerations based on the multiplanar configuration of the *cyclo*heptane ring lead to the view that only small differences in strain are again involved. However, the *cyclo*heptane ring is endowed with greater mobility than the *cyclo*hexane ring, and it is probable that these results are explained by the fact that, although the difference in the strains in the two stereoisomeric modifications is small, the great mobility of the 7-membered ring leads to the formation, almost exclusively, of the less strained isomeride.



(IV.)



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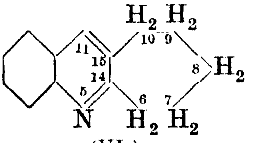

(VI.)

S. Fujise [81] has obtained two of the four possible 8-hydroxydecahydroquinolines by the hydrogenation of 8-hydroxyquinoline in acetic acid with platinum-black at 40—45°. A third stereoisomeride results from either of the first two by heating the sodium derivative. The same author [82] has prepared *cis*- and *trans*-2-dimethylamino-*n*-propyl*cyclo*hexane by the catalytic reduction of the bases obtained by the Hofmann degradation process from *cis*- and *trans*-decahydroquinoline,[83] respectively. These results have been used [84] to prove that the catalytic hydrogenation of 2-methylindole in glacial acetic acid at 40—45° leads to the *cis*-modification of 2-methyloctahydroindole, since the product, by a similar process, gave *cis*-2-dimethylamino-*n*-propyl*cyclo*hexane.

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[79] *J.*, 1928, 2583.

[80] Compare also W. H. Perkin and W. G. Sedgwick, *J.*, 1924, **125**, 2437.

[81] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, **8**, 161; **A.**, 898.

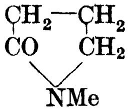
[82] *Ibid.*, p. 185; **A.**, 1022.

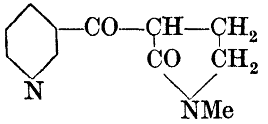
[83] Compare W. Huckel and F. Stepf, *Annalen*, 1927, **453**, 163.

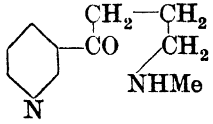
[84] S. Fujise, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, **9**, 91; **A.**, 1258.

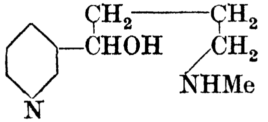
Alkaloids.

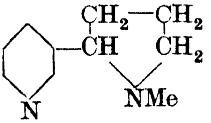
Nicotine.—E. Späth and H. Bretschneider [85] have developed an interesting new synthesis of nicotine, which has some advantages over the older Pictet synthesis since it avoids the drastic temperature conditions of the latter. Ethyl pyridine-3-carboxylate condenses with 1-methyl-2-pyrrolidone (I) in the presence of sodium ethoxide to give (II), which, on heating with fuming hydrochloric acid, gives the amino-ketone (III) by hydrolysis and loss of carbon dioxide. This is reduced to the secondary alcohol (IV) by boiling


(I.)


(II.)

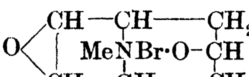

(III.)

(IV.)



(V.)

with zinc dust in alcoholic alkaline solution; and the corresponding iodide, obtained by heating with fuming hydriodic acid, yields *dl*-nicotine (V) with aqueous alkali.

Tropane Group.—M. Polonovski and M. Polonovski [86] have found that the action of hydrogen peroxide on scopolamine (hyoscine) not only leads to the amine-oxide, but also yields scopinium hydroxide, which was isolated as its bromide (VI). On reduction with zinc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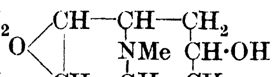
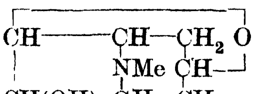

(VII.)


(VIII.)

and hydrochloric acid, or with sodium amalgam, this gives ψ-scopine, which is regarded as having the structure (VII) and as being a stereoisomeride of scopine, the relationship being similar to that existing between tropine and ψ-tropine. The properties of ψ-scopine preclude the possibility of its being a stereoisomeride of scopoline (oscine) (VIII).

Aporphine Group.—J. M. Gulland and R. D. Haworth,[87] by using phosphorus pentachloride in cold chloroform solution, have overcome the difficulties previously encountered [88] in attempts to prepare 2′-nitro-1-benzyl-3 : 4-dihydro*iso*quinoline (X; R = H) derivatives from the corresponding substituted 2′-nitrophenylaceto-β-phenylethylamides (IX; R = H), and a route for the synthesis of naturally occurring derivatives of aporphine (XII; R = H) has been developed. Thus 2′-nitro-6 : 7-dimethoxy-1-benzyl-3 : 4-dihydro*iso*quinoline (X; R = MeO) has been synthesised from 2′-nitrophenylaceto-β-3 : 4-dimethoxyphenylethylamide (IX; R = MeO). The methiodide of this base, on reduction with zinc dust and hydrochloric acid in *strongly* acid solution, yielded 2′-amino-6 : 7-dimethoxy-1-benzyl-2-methyltetrahydro*iso*quinoline (XI), from which 5 : 6-dimethoxyaporphine (XII; R = MeO) was obtained either by diazotising it in 2*N*-sulphuric acid and adding copper powder, or by diazotising it in a mixture of methyl alcohol and 2*N*-sulphuric acid and then heating the solution. The corresponding phenol and the dilaudanosine derivative were also formed at the same time. During the reduction of the methiodide of the above base (X; R = MeO), a small quantity of a compound which appears to be 2-(4′ : 5′-dimethoxy-2′-β-methylaminoethyl)phenyldihydroindole (XIII) was also formed. Reduction of the same methiodide with zinc dust and dilute sulphuric acid in *weakly* acid solution yielded a compound which is thought to be 2-(4′ : 5′-dimethoxy-2′-β-methylaminoethyl)phenylindole (XIV).

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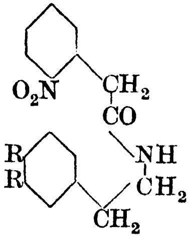
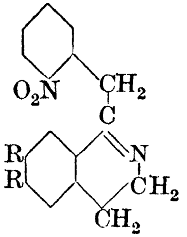
[85] *Ber.*, 1928, **61**, [*B*], 327; **A.**, 431.

[86] *Compt. rend.*, 1927, **185**, 277; 1928, **186**, 147; *Bull. Soc. chim.*, 1928, [iv], **43**, 79, 590; **A.**, 1927, 888; 1928, 310, 908

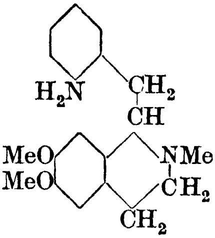
[87] *J.*, **1928**, **581**.



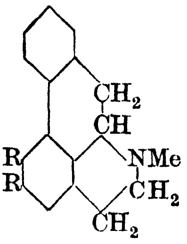
(IX.)



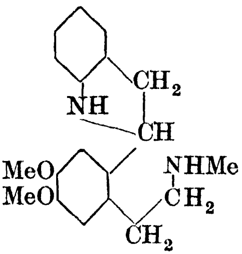
(X.)



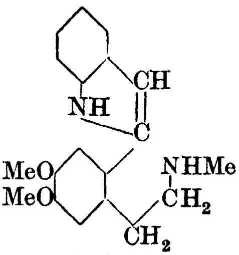
(XI.)



(XII.)



(XIII.)



(XIV.)

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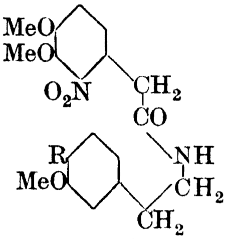
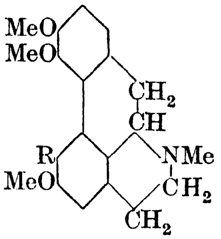
[88] A. Pictet and F. W. Kay, *J.*, 1913, **103**, 950; J. Gadamer, M. Oberlin, and A. Schoeler, *Arch. Pharm.*, 1925, **263**, 81; *A.*, 1925, i, 576.

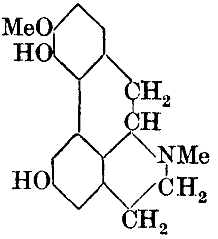
By a series of reactions similar to those used for preparing 5 : 6-dimethoxyaporphine, 2′-nitro-3′ : 4′-dimethoxyphenylaceto-β-3 : 4 dimethoxyphenylethylamide (XV ; R = MeO) has been converted by J. M. Gulland and R. D. Haworth [89] into 3 : 4 : 5 : 6-tetramethoxyaporphine (XVI; R = MeO). The *d*-form of this base is undoubtedly identical with the corytuberine dimethyl ether (corydine and *iso*corydine monomethyl ether) obtained by J. Gadamer [90] from naturally occurring *d*-corytuberine, and this synthesis confirms the structure which Gadamer suggested. E. Späth and O. Hromatka [91] also have synthesised *d*-corytuberine dimethyl ether by a series of reactions which are essentially the same as these, although phosphoric oxide was used to convert the amide into the *iso*quinoline.



(XV.)



(XVI.)



(XVII.)

By a further application of these reactions to 2′-nitro-3′ : 4′-dimethoxyphenylaceto-β-3-methoxyphenylethylamide (XV ; R = H), J. M. Gulland and R. D. Haworth [92] have synthesised 3 : 4 : 6-trimethoxyaporphine (XVI; R = H), the *l*-form of which is identical with morphothebaine dimethyl ether. The structure (XVII) assigned to morphothebaine (obtained by the action of hot concentrated hydrochloric acid on thebaine) by R. Pschorr and W. L. Halle [93] is supported by this synthesis of its dimethyl ether.

By various processes of oxidation E. Späth, H. Holter, and R. Posega [94] have confirmed the structure (XVIII; R = H) previously assigned by J. Gadamer and F. Kuntze [95] to bulbocapnine. For instance, by heating the methiodide of the methine base obtained by the Emde degradation of bulbocapnine with concentrated nitric acid, benzene-1 : 2 : 3 : 4-tetracarboxylic acid was obtained. Oxidation of bulbocapnine with potassium permanganate gave oxyhydrastinine (XIX), bulbocapnine methyl ether yielded hemipinic acid and 2 : 3-methylenedioxy-2′ : 3′-dimethoxydiphenyl-5 : 6 : 6′-tricarboxylic acid, and bulbocapnine ethyl ether gave 4-methoxy-3-ethoxyphthalic acid. The latter result established the relative positions of the hydroxy- and methoxy-groups, but the unlikely possibility that they are in the 1 : 2 positions respectively in the nucleus still remained. This possibility was disposed of and the constitution assigned to bulbocapnine was further confirmed by the synthesis of *dl*-bulbocapnine methyl ether (XVIII; R = Me) by J. M. Gulland and R. D. Haworth [96] from 2′-nitro-3′ : 4′-dimethoxyphenylaceto-β-3 : 4-methylenedioxyphenylethylamide (XX) by a process similar to that used for those aporphine derivatives already mentioned. E. Späth and O. Hromatka [97] also have synthesised bulbocapnine methyl ether by reactions which are practically the same as these.

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[89] *J.*, 1928, 1834.

[90] *Arch. Pharm.*, 1911, **249**, 547.

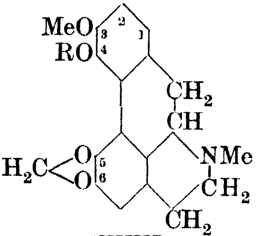
[91] *Ber.*, 1928, **61**, [*B*], 1692 ; **A.**, 1265.

[92] *J.*, 1928, 2083.

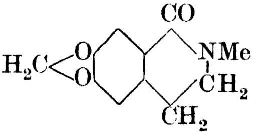
[93] *Ber.*, 1907, **40**, 2004.

[94] *Ber.*, 1928, **61**, [*B*], 322; **A.**, 432.

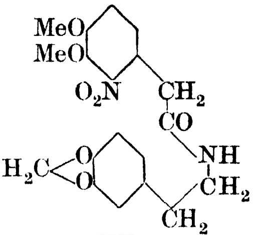
[95] *Arch. Pharm.*, 1911, **249**, 598.



(XVIII.)

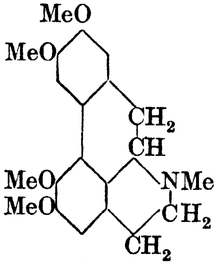


(XIX.)

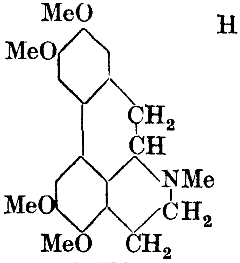


(XX.)

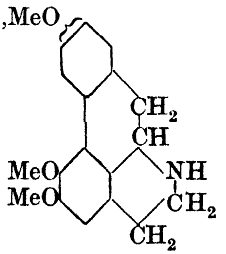
K. Gorter [98] previously claimed to have converted laurotetanine, the alkaloid from various *Lauraceæ*, by methylation with diazomethane into an *N*-methyl-laurotetanine methyl ether, which was regarded as very similar to, but not identical with, glaucine (XXI), the structure of which has been established by synthesis.[99] This dimethyl derivative of laurotetanine was called *iso*glaucine, and the structure (XXII) was assigned to it. E. Späth and F. Strauhal [1] have now shown that methylation of laurotetanine with diazomethane really yields a mixture of laurotetanine *O*-methyl



(XXI.)



(XXII.)



(XXIII.)

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[96] *J.*, 1928, 1132.

[97] *Ber.*, 1928, **61**, [*B*], 1334; **A.**, 908.

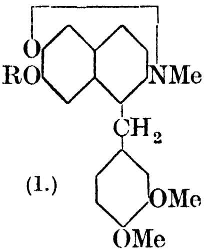
[98] *A.*, 1921, i, 587.

[99] J. Gadamer, *Arch. Pharm.*, 1911, **249**, 680.

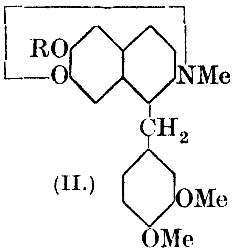
[1] *Ber.*, 1928, **61**, [*B*], 2395.

ether and glaucine. Gorter's observation that oxidation of laurotetanine with alkaline permanganate yields 1 : 2-dimethoxybenzene-3 : 4 : 5-tricarboxylic acid has been confirmed; two methoxyl groups must therefore be in that benzene ring which is attached to three carbon atoms, and the alkaloid possesses the formula (XXIII). The presence of the phenanthrene nucleus has been demonstrated by oxidation with nitric acid to benzene-1 : 2 : 3 : 4-tetracarboxylic acid of the base obtained from the fully methylated alkaloid by the Emde degradation. G. Barger and R. Silberschmidt [2] have also found that Gorter's *iso*glaucine is identical with glaucine by examining the products of the Hofmann degradation process from both.

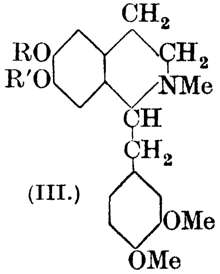
1-*Benzyl*iso*quinolines.*—In a continuation of the work of E. Späth and his collaborators on the minor opium alkaloids [3] it has been found [4] that the thermal decomposition of papaverine hydrochloride yielded (*a*) protopapaverine (I; R = H, 41%), (*b*) the hydrochloride of a base (I; R = Me, 29%), (*c*) a compound (II; R = Me, 10%), and (*d*) the substance (II; R = H, about 10%).



(I.)



(II.)



(III.)

The constitution now assigned to protopapaverine [5] is indicated by the following facts : (i) it contains only two methoxyl groups and a methylimino-group; (ii) it is soluble in alkalis; (iii) it is not a partly demethylated papaverine, since the latter could not be formed from it with diazomethane; (iv) oxidation by permanganate gave veratric acid; (v) reduction with tin and hydrochloric acid, followed by methylation with diazomethane, yielded *dl*-laudanosine (III; R = R′ = Me); and (vi) methylation of protopapaverine with diazomethane gave the substance (*b*), which was reduced to *ψ*-laudanine (III; R = H; R′ = Me). Protopapaverine with methyl iodide yielded 7-hydroxy-6 : 3′ : 4′-trimethoxybenzyl*iso*quinoline methiodide. The corresponding methochloride was reduced by tin and hydrochloric acid to *dl*-codamine (III; R = Me;

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[2] *J.*, 1928, 2919.

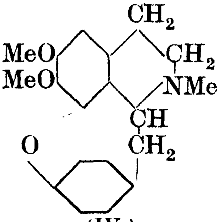
[3] Compare *Ann. Reports*, 1926, **23**, 164.

[4] E. Späth and H. Epstein, *Ber.*, 1928, **61**, [*B*], 334; **A.**, 432.

[5] Compare A. Pictet and G. H. Kramers, *A.*, 1903, i, 358; O. Hesse, *J. pr. Chem.*, 1903, **68**, 199.

R′ = H), which gave *dl*-laudanosine with diazomethane. The substances (*c*) and (*d*) were isolated as their reduction products, *dl*-codamine and the corresponding 6 : 7-dihydroxy-compound, respectively.

E. Späth, W. Leithe, and F. Ladeck [6] have shown that curine, from Para curare, is identical with bebeerine (α-chondodendrine), from the root "Pareira brava," an alkaloid which has hitherto received little attention. Some of the earlier work on curine is now considered to be untrustworthy, and it is suggested that the methyl ether of this alkaloid may be represented by the formula (IV). In curine there is a methyl group attached to the nitrogen atom, a methoxyl and a phenolic hydroxyl group, and the third oxygen atom appears to be of the ether type and to be present in a *p*-hydroxybenzyl residue. Oxidation of curine yielded traces of *p*-hydroxybenzoic acid, but no *p*-anisic acid resulted from its methyl ether on similar treatment. Zinc dust distillation yielded 1-methyl*iso*quinoline, suggesting that the *p*-hydroxybenzyl group is joined to the *iso*quinoline nucleus in the 1-position. The three oxygen atoms, which must be attached to the benzene portion of the tetrahydro*iso*quinoline skeleton, are thought to occupy the 6, 7, and 8 positions, although there is as yet no certainty about this.



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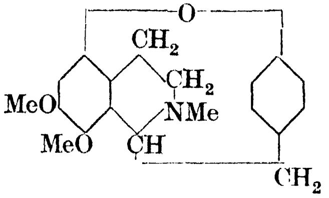

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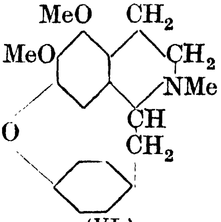

(VI.)

Further work has also been carried out by F. Faltis and A. Troller [7] with the related, isomeric alkaloid, *iso*chondodendrine (*iso*bebeerine). Previously F. Faltis and F. Neumann [8] suggested the structure (V) for the methyl ether of this alkaloid as a result of an examination of the oxidation product of a substance, $C_{18}H_{16}O_3$, which was obtained from this methyl ether by the Hofmann degradation process. A more detailed investigation of this oxidation product, a tricarboxylic acid of the formula $C_{12}H_5O(OMe)_2(CO_2H)_3$, has indicated that it is not identical with 3-*p*-carboxyphenoxy-5 : 6-dimethoxyphthalic acid (VII) as was originally believed. Demethylation of the tricarboxylic acid gave a pyrocatechol derivative with simultaneous loss of one carboxyl group, and this product, after remethylation, has now been shown by synthesis

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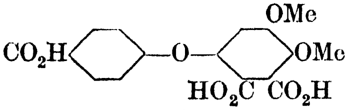
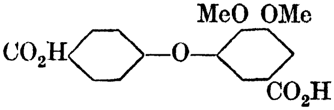
[6] *Ber.*, 1928, **61**, [*B*], 1698; **A.**, 1264.

[7] *Ber.*, 1928, **61**, [*B*], 345; **A.**, 433.

[8] *Monatsh.*, 1921, **42**, 311; *A.*, 1922, i, 569.



(VII.)



(VIII.)

to be 3-*p*-carboxyphenoxy-4 : 5-dimethoxybenzoic acid (VIII). The methyl ether of *iso*chondodendrine, therefore, is probably now represented by the formula (VI).

Diisoquinoline Group.—In recent years it has become practically certain that corydaline, the main alkaloid in *Corydalis cava* and *Corydalis tuberosa*, has the formula (I) and not the isomeric structure (II) suggested by J. J. Dobbie and A. Lauder.[9] Confirmation of

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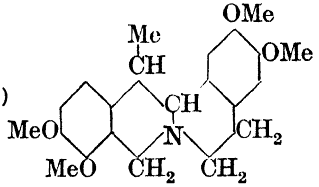
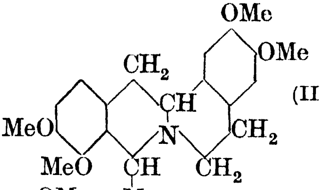
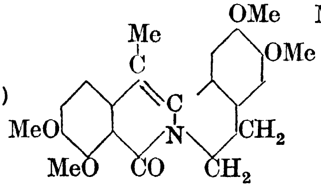


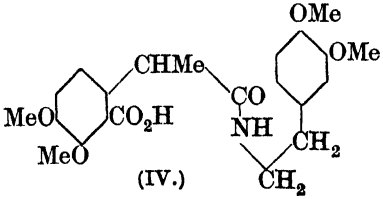


(II.)

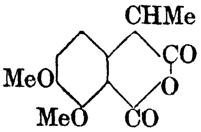
(III.)



this has resulted from the synthesis of oxydehydrocorydaline (III) by J. B. Koepfli and W. H. Perkin.[10] *N*-β-Veratrylethyl-3 : 4-dimethoxy-α-methylhomophthalamic acid (IV), produced by the action of β-veratrylethylamine on 3 : 4-dimethoxy-α-methylhomophthalic anhydride (V) in benzene solution, was converted into its methyl ester and then dehydrated with phosphorus oxychloride to yield (VI), which gave oxydehydrocorydaline by loss of methyl



(IV.)



(V.)

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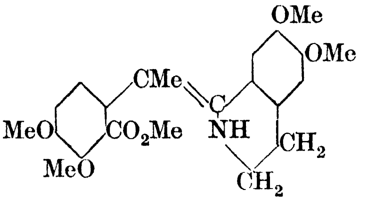
[9] *J.*, 1902, **81**, 148. Compare *Ann. Reports*, 1927, **24**, 170.

[10] *J.*, 1928, 2989.

alcohol, when heated at 150—170°.[11] This product proved to be identical with the oxydehydrocorydaline which is obtained from dehydrocorydaline, the base formed by mild oxidation of corydaline, by treating its acetate with sodium hydroxide.[12]



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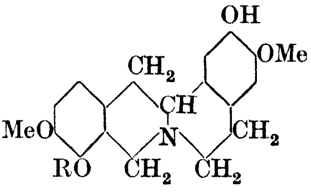
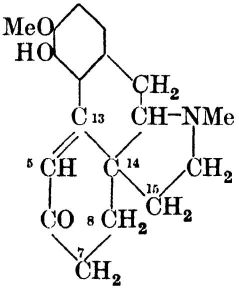


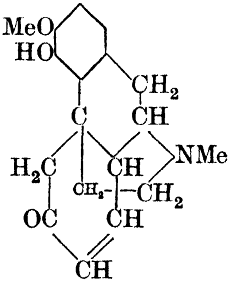
(VII.)

J. Gadamer, E. Späth, and E. Mosettig[13] have investigated the two new alkaloids isolated by Knorck[14] from *Corydalis cava*, and have shown that one (m. p. 240—241°) is *iso*corypalmine (2-hydroxy-3 : 9 : 10-trimethoxytetrahydroprotoberberine) (VII; R = Me). The other (m. p. 192—193°) contains only two methoxyl groups and its reactions indicate that it is 2 : 9-dihydroxy-3 : 10-dimethoxytetrahydroprotoberberine (VII; R = H).

Morphine Group.—C. Schöpf and F. Borkowsky[15] have adopted the formula (I) for thebainone in the place of those put forward by J. M. Gulland and R. Robinson[16] (II and III, of which II is preferred). The existence of the C^{13}—C^{15} linkage (as in formula II) is ruled out by the isolation of dihydroepithebainoneoxime by the catalytic hydrogenation of thebaine. This oxime is isomeric, but not identical, with dihydrothebainoneoxime, and also with thebainoloxime. The presence of the double linkage in the 5 : 13



(I.)



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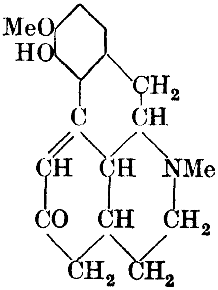

(III.)

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[11] Compare the synthesis of oxypalmatine by R. D. Haworth, J. B. Koepfli, and W. H. Perkin, *J.*, 1927, 548.

[12] J. Gadamer and F. von Bruchhausen, *Arch. Pharm.*, 1922, **259**, 249.

[13] *Ibid.*, 1927, **265**, 675; **A.**, 1928, 310.

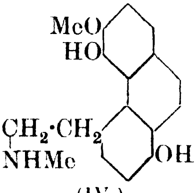
[14] *Diss.*, Marburg, 1926.

[15] *Annalen*, 1927, **458**, 148; **A.**, 1927, 1209.

[16] *J.*, 1923, **123**, 998.

position is considered to explain the properties of thebainone better than when in the 7 : 8 position, and the degradation reactions in this series suggest a C^{14}—C^{15}, rather than a C^{8}—C^{15} (formula III), linkage.

Although the mechanism of the remarkable changes by which thebaine and codeinone are converted into thebenine (IV), on heating with dilute hydrochloric acid, is still not clear, the constitution assigned to the latter substance has been confirmed by J. M. Gulland and C. J. Virden.[17] By catalytic hydrogenation of 3 : 4 : 8-trimethoxy-5-vinylphenanthrene, obtained by the action of aqueous sodium hydroxide on the methosulphate of the fully methylated derivative of thebenine, 3 : 4 : 8-trimethoxy-5-ethylphenanthrene (V) was produced. *trans*-α-(6′-Methoxy-3′-ethylphenyl)-2-nitro-3 : 4-dimethoxycinnamic acid (VI), from 2-nitroveratraldehyde and sodium 6-methoxy-3-ethylphenylacetate, yielded, with ferrous sulphate and ammonia, the corresponding amine, which by a diazo-reaction gave 3 : 4 : 8-trimethoxy-5-ethylphenanthrene-9-carboxylic acid. The elimination of carbon dioxide from this acid gave (V), identical with the product from thebenine.



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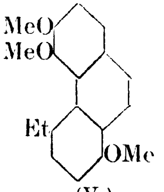

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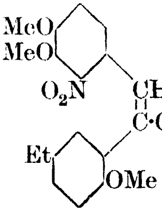
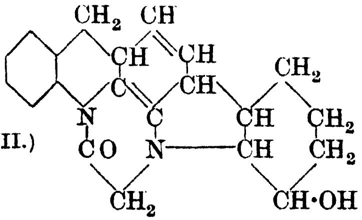
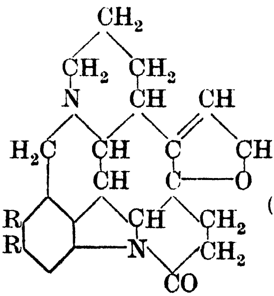


(VI.)

Strychnine and Brucine.—A very interesting development in the extremely complex problem of the constitutions of strychnine and brucine has been the advent of a new structural formula, put forward by R. C. Fawcett, W. H. Perkin, and R. Robinson.[18] It has long been realised that the earlier strychnine formula (VII) of W. H. Perkin and R. Robinson [19] could no longer serve, and the

(VII.)





(VIII.)

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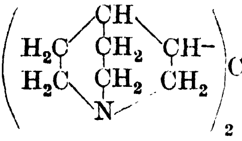
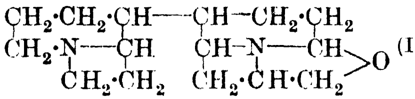
[17] *J.*, 1928, 921.
[18] *Ibid.*, p. 3082.
[19] *J.*, 1910, **97**, 305.

present formula (VIII; strychnine, R = H; brucine, R = MeO) is suggested on the view that dinitrostrychol is a dinitrodihydroxy-*iso*quinoline and not a quinoline derivative, as hitherto believed, and the carbazole nucleus is still retained. It is not possible in the space available to give an adequate *résumé* of the reactions of these alkaloids in the light of the new formula, but it may be mentioned that, as the authors point out, the constitutions given may require certain re-adjustments, which do not affect their fundamental character.

Lupin Alkaloids.—Much work has been devoted to the problems concerning the structures of the alkaloids from *Lupinus* spp. K. Winterfeld [20] has succeeded in controlling the oxidation of sparteine, $C_{15}H_{26}N_2$, by using mercuric acetate in dilute acetic acid. In the cold, dehydrosparteine, $C_{15}H_{24}N_2$, is produced, but at a higher temperature dehydrogenation proceeds further to give didehydrosparteine, $C_{15}H_{22}N_2$. The study of these products has not yet reached a stage at which definite deductions concerning the constitution of sparteine can be drawn, but this stepwise dehydrogenation seems to be inconsistent with the symmetrical formula (I) of C. Moureu and A. Valeur.[21]

(I.)





(II.)

Previous work on the alkaloid lupanine, $C_{15}H_{24}ON_2$, has led to very little evidence of any value in assigning a constitution, but H. Thoms and K. Bergershoff [22] have put forward the provisional formula (II). G. R. Clemo and Miss G. C. Leitch [23] have found that, although a dihydrochloride can be obtained, lupanine gives only a monomethiodide and a monomethosulphate. This methiodide is comparatively stable and degradation was only possible under vigorous conditions. The product obtained by heating with a mixture of caustic soda and caustic potash in a vacuum contained two methyl-lupanines, whereas the use of caustic potash alone yielded a mixture of simpler bases, which have not yet been identified. Reduction of lupanine with hydriodic acid and red phosphorus at 220° gave deoxylupanine, $C_{15}H_{26}N_2$, which is isomeric with sparteine. Deoxylupanine and sparteine, although not identical, are apparently closely related and both may, therefore, contain the quinuclidine ring system, which is unaffected by these reducing conditions. Both bases are easily oxidised to *iso*lupanine and oxysparteine respectively. Previous attempts to oxidise lupanine have given no useful result, but G. R. Clemo and Miss G. C. Leitch have now converted the alkaloid by potassium permanganate in acetone into oxylupanine, $C_{15}H_{22}O_2N_2$, which contains no reactive carbonyl, methylene, or hydroxyl group, and no reactive tertiary nitrogen atom.

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[20] *Arch. Pharm.*, **1928**, **266**, 299; **A.**, 906.

[21] *Compt. rend.*, **1905**, **141**, 117.

[22] *Arch. Pharm.*, **1925**, **263**, 1. Compare *Ann. Reports*, 1927, **24**, 193.

[23] *J.*, **1928**, 1811.

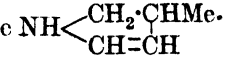
C. Schöpf and his co-workers [24] have investigated lupininic acid from the oxidation of the alkaloid lupinine, $C_{10}H_{19}ON$, with chromic acid, and, from a study of some of its derivatives in the light of the reactions of the cinchona alkaloids, the view has been expressed that a quinuclidine structure for lupinine is unlikely.

Minor Alkaloids.—Continuing an investigation of the alkaloids from *Ephedra* species,[25] S. Smith [26] has isolated from the Chinese drug Ma Huang a fourth alkaloid, nor-*d*-*ψ*-ephedrine,

$$OH{\cdot}CHPh{\cdot}CHMe{\cdot}NH_2,$$

and has described its properties.

A. Pictet and R. Pictet [27] have found that the volatile alkaloid, C_5H_9N, obtained by steam-distilling black pepper gives an oily nitrosoamine and is reduced by tin and hydrochloric acid to *dl*-3-methylpyrrolidine. The alkaloid is, therefore, 3-methylpyrroline, and, since it is optically active, it has the structure



$NH\!<\!\begin{matrix}CH_2{\cdot}CHMe{\cdot}\\ CH{=}CH\end{matrix}$

The suggestion that vasicine, an alkaloid from *Adhatoda vasica*, is 2-propyl)or *iso*propyl)-4-hydroxyquinazoline [28] has been shown to be incorrect. A. K. De and J. N. Ray [29] have now prepared these two substances by condensing butyranilide and *iso*butyranilide with ethyl carbamate in boiling xylene in the presence of phosphoric oxide, and have found that the natural product differs from both of them.

Tellurium Ring Compounds.

Some interesting series of compounds in which tellurium is present as part of a ring system have been investigated in the past few years. The action of tellurium tetrachloride on β-diketones leads to the *cyclo*telluripentane-3 : 5-dione 1 : 1-dichlorides (I), which can be reduced with aqueous potassium metabisulphite to the *cyclo*telluropentane-3 : 5-diones (II).[30] The structure assigned to these substances, which have pronounced bactericidal action, is confirmed by the fact that the *cyclo*telluropentane-3 : 5-diones can yield, in general, both mono- and di-oximes. *cyclo*Telluropentane

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[24] *Annalen*, 1928, **465**, 97; **A.**, 1144.

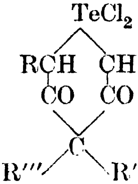
[25] Compare *Ann. Reports*, 1927, **24**, 195.

[26] *J.*, 1928, 51.

[27] *Helv. Chim. Acta*, 1927, **10**, 593; **A.**, 1927, 1208.

[28] T. P. Ghose, *J. Indian Chem. Soc.*, 1927, **4**, 1; *Ann. Reports*, 1927, **24**, 194.

[29] *J. Indian Chem. Soc.*, 1927, **4**, 541; **A.**, 1928, 428.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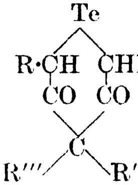
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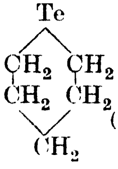
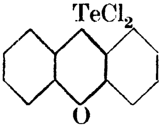

(III.)

(III), which may be regarded as the parent of this group of compounds, has been prepared by G. T. Morgan and H. Burgess[31] by heating aluminium telluride with an αε-pentamethylene dihalide. The first product of the reaction is a mixture of telluronium salts, formed by further addition of the pentamethylene dihalide, but these can be converted into *cyclo*telluripentane-1 : 1-dibromide, which is then reduced with aqueous potassium metabisulphite.

H. D. K. Drew[32] has found that when diphenyl ether reacts with tellurium tetrachloride it gives, first, *p*-phenoxyphenyltelluritrichloride, $PhO \cdot C_6H_4 \cdot TeCl_3$, but this product, on heating to 200°, yields, apparently through intermediate migration of the $-TeCl_3$ group to the *o*-position, 10 : 10-dichlorophenoxtellurine (IV), which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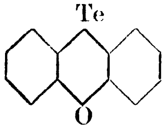
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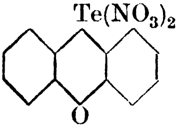
(VI.)

is easily reduced to phenoxtellurine (V) with aqueous potassium metabisulphite. The tellurium atom can be removed from phenoxtellurine and its nitro- and amino-derivatives by the action of boiling aqueous potassium hydroxide on the 10 : 10-dichlorides; potassium tellurite and the corresponding derivatives of diphenyl ether are then produced.[33] With bromine or iodine, phenoxtellurine gives 10 : 10-dibromo- or 10 : 10-di-iodo-phenoxtellurine, and the action of warm nitric acid leads to the colourless 10 : 10-dinitrate (VI) through an intermediate bluish-violet phase. Phenoxtellurine also dissolves in sulphuric acid with the formation of highly coloured complexes which can be isolated under suitable conditions : the same coloured salts can be formed from the pale yellow phenoxtellurine dibisulphate trihydrate (VII) by combination with phenoxtellurine. It is probable that these highly coloured tellurylium salts, which may also occur with other anions,

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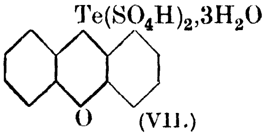
[30] G. T. Morgan and H. D. K. Drew, *J.*, 1920, **117**, 1456; 1924, **125**, 731, 1601.

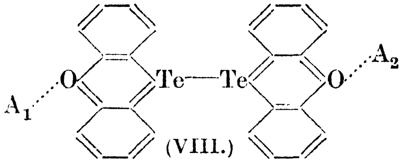
[31] *J.*, 1928, 321.

[32] *J.*, 1926, 223.

[33] H. D. K. Drew and R. W. Thomason, *J.*, 1927, 116.

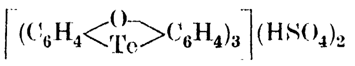


(VII.)



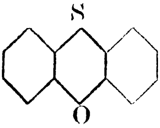
(VIII.)

have structures of the type (VIII ; A_1 and A_2 = HSO_4, ClO_4, NO_3, or H_2PO_4), and a more complex structure (IX) is also represented.[34]

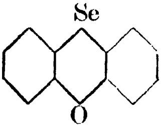


$$\left[(C_6H_4{<}^{O}_{Te}{>}C_6H_4)_3\right](HSO_4)_2$$

(IX.)



(X.)



(XI.)

Phenoxthionine (X) and phenoxselenine (XI) can be obtained from phenoxtellurine by heating with one atomic proportion of sulphur or selenium respectively. There is evidence that the colours produced by dissolving phenoxthionine and phenoxselenine derivatives in sulphuric acid are due to the formation of thionylium and selenylium salts analogous to the tellurylium compounds mentioned above.[35]

S. G. P. PLANT.

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[34] H. D. K. Drew, *J.*, 1926, 3054; 1928, 506.

[35] *Idem*, *J.*, 1928, 511.

ANALYTICAL CHEMISTRY.

Definite advances in analytical practice have been recorded during the year. Microchemical tests for various elements are now attaining considerable importance, particularly for some of the rarer elements such as gallium, indium, and rubidium. The difficulties attending the analytical separation and estimation of tantalum and niobium may now be said to be overcome to a large extent by the use of the tannic acid method of separation, and the troublesome separation of beryllium from aluminium is now practically solved.

A considerable amount of work has been devoted to the accurate determination of minute quantities of arsenic by the Gutzeit method. This work has been largely directed to prescribing the exact conditions essential for obtaining uniform results.

Many papers dealing with potentiometric methods have appeared, and the ease of utilising the method in practice is again demonstrated by the extensive literature on oxidation–reduction methods. The difficulty underlying the use of alkali ferrocyanides when determining the end-point potentiometrically in precipitation reactions has also been extensively investigated. This useful reaction has accordingly been extended in several directions where ordinary methods. of titration are clumsy or difficult to apply. Ceric sulphate in acid solutions is found to be a very useful reagent in potentiometric work, as will be gathered from its application to the determination of vanadium in steel and to its use in determining nitrites and peroxides amongst many other substances. An advantage of ceric sulphate solutions is their stability when properly stored. The use of various metallic electrodes potentiometrically is extending with both "indicator" electrodes and "reference" electrodes, tungsten being found very useful in the latter class.

A few investigators have taken up the consideration of two important matters often neglected, *viz.*, the adequacy of sampling in practice, and the incidence of unavoidable errors in analytical methods.

Inorganic Analysis.

Qualitative.—The formation of an insoluble reddish-violet salt with *p*-dimethylaminobenzylidenerhodanine, preferably in the presence of carbon disulphide to act as solvent for excess of reagent, constitutes[1] a specific test for silver, far more delicate than the chloride reaction. In more concentrated solutions the characteristic rhombic crystals of the sulphate serve for the microchemical detection of silver.[2] Further spot-tests on filter paper, referred to in recent Reports, embrace lead,[3] silver, copper, mercury, chromium, and manganese.[4] Lead, bismuth, copper, mercury, and silver are removed from acid solution by iron or zinc powder prior to testing for cadmium.[5]

Cathodic deposition of lead, which is promoted by the presence of phosphoric acid, is not so delicate or satisfactory a qualitative test as anodic deposition followed by the colour reaction with tetramethyldiaminodiphenylmethane; of the metals bismuth, mercury, iron, copper, cadmium, and manganese, the last alone interferes.[6] The red coloration afforded by careful mixing of a stannous solution with acidified diazine-green-S is a delicate test for tin.[7]

Diphenylcarbazide is much preferred to hydrogen peroxide and ether as a reagent for chromium as chromate.[8] The test for iron with dimethylglyoxime and hydrogen sulphide is, under certain conditions, about as sensitive as that with thiocyanate.[9]

The reactions of cobalt, both alone and also in the presence of nickel and zinc, are described.[10] Delicate colour reactions for zinc are given, metanil-yellow, orange-IV, or diethylaniline being used in conjunction with potassium ferricyanide.[7]

Magnesium salts which can be decomposed by sodium hydroxide are coloured reddish-violet when treated with an alcoholic solution of diphenylcarbazide.[11] Dolomite does not give the reaction unless previously heated to redness. From this fact the mineral is formulated as calcium magnesocarbonate, which is stated to be supported by *X*-ray analysis.[12] A sensitive colour reaction for magnesium, applicable in the presence of fairly large proportions of calcium, is given by Clayton-yellow followed by alkali.[13] Concentrated zirconium sulphate is a fairly sensitive reagent for potassium in the presence of sodium.[14] It is more useful in the presence of ammonium salts which interfere with most other tests.[15] The use of uranyl acetate as a reagent in microscopical analysis is described for a number of metals.[16] The delicacy of the formation of sodium zinc uranyl acetate is so great that silica object slides should be used instead of ordinary glass.

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[1] F. Feigl, *Z. anal. Chem.*, 1928, **74**, 380; **A.**, 1108.

[2] O. Hackl, *Mikrochem.*, 1928, **6**, 106; **A.**, 980.

[3] N. A. Tananaev, *Z. anorg. Chem.*, 1927, **167**, 81; **A.**, 1927, 1161.

[4] N. A. Tananaev and I. Tananaev, *ibid.*, 1928, **170**, 113; **A.**, 500.

[5] P. G. Popov, *Ukraine Chem. J.*, 1928, **3**, 153, 158; **A.**, 1206.

[6] P. W. Danckwortt and E. Jurgens, *Arch. Pharm.*, 1928, **266**, 367; **A.**, 981.

[7] E. Eegriwe, *Z. anal. Chem.*, 1928, **74**, 225; **A.**, 982.

[8] N. M. Stover, *J. Amer. Chem. Soc.*, 1928, **50**, 2363; **A.**, 1206.

[9] R. Nakaseko, *Mem. Coll. Sci. Kyōtō*, 1928, *A*, **11**, 113; **A.**, 727.

[10] H. Fischer, *Wiss. Veröff. Siemens-Konz.*, 1928, **6**, (2), 147; **A.**, 727.

[11] F. Feigl, *Z. anal. Chem.*, 1927, **72**, 113; **A.**, 1927, 1161; F. Feigl and H. Leitmeyer, *Zentr. Min. Geol.*, 1928, *A*, 74; **A.**, 1206.

[12] F. Feigl, *Z. anal. Chem.*, 1928, **74**, 398; **A.**, 1108.

[13] H. D. Barnes, *J.S. African Chem. Inst.*, 1928, **11**, 67; **A.**, 1108.

The removal of phosphoric acid as the lead salt in qualitative testing is described.[17] Hexamethylenetetramine with ammonium thiocyanate and piperazine with sodium iodide or bromide are used as microchemical reagents for a number of metals.[18]

The formation of characteristic black crystals of a complex iodide with silver and gold serves to detect very small quantities of rubidium in the presence of sodium, potassium, or ammonium salts but cæsium interferes.[19] A series of microchemical tests, investigated to avoid the possible interference of other elements likely to be present in minerals, has been described for iron, gallium, indium, palladium,[20] tellurium, selenium, manganese,[21] gold, and sulphur.[22] Quadrivalent iridium and osmic acid solutions give with benzidine blue colorations.[23] In the absence of gold, copper, selenium, and the platinum metals, the reduction of tellurates and tellurites by titanous chloride in hydrochloric acid solution serves as a test for tellurium.[24] For the detection of vanadate, it is recommended to precipitate the vanadium with the metals of the iron group; hot sodium hydroxide then extracts from the washed precipitate vanadium together with aluminium.[25] Soluble vanadates, tungstates, and molybdates form with pyrocatechol acetate followed by aniline or piperazine characteristic coloured precipitates.[26] Curcumin gives with beryllium salts in ammoniacal solution a reddish flocculent precipitate, but aluminium and ferric iron must first be precipitated by addition of sodium fluoride.[27]

[14] R. D. Reed and J. R. Withrow, *J. Amer. Chem. Soc.*, 1928, **50**, 1515; **A.**, 858.

[15] *Idem, ibid.*, p. 2985.

[16] E. M. Chamot and H. A. Bedient, *Mikrochem.*, 1928, **6**, 13; **A.**, 385.

[17] G. G. Kandilarov, *Z. anal. Chem.*, 1927, **72**, 263; **A.**, 1928, 144.

[18] A. Martini, *Mikrochem.*, 1928, **6**, 28; **A.**, 387.

[19] E. S. Burkser and S. G. Rublof, *Ukraine Chem. J.*, 1926, **2**, 355; *Mikrochem.*, 1927, **5**, 137; **A.**, 1928, 37.

[20] P. C. Putnam, E. J. Roberts, and D. H. Selchow, *Amer. J. Sci.*, 1928, (v), **15**, 423; **A.**, 727.

[21] *Idem, ibid.*, p. 253; **A.**, 498. [22] *Idem, ibid.*, p. 455; **A.**, 861.

[23] V. G. Chlopin, *Ann. Inst. Platine*, 1926, **4**, 324; **A.**, 1927, 1162.

[24] O. Tomiček, *Bull. Soc. chim.*, 1927, (iv), **41**, 1399; **A.**, 1928, 36.

[25] J. Röll, *Z. anal. Chem.*, 1928, **74**, 342; **A.**, 983.

[26] A. Martini, *Mikrochem.*, 1928, **6**, 63; **A.**, 387.

[27] I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1928, **50**, 393; **A.**, 386.

Vigorous evolution of nitrogen from a solution containing sodium azide and iodine is induced by the addition of sulphide and thiosulphate, but not by other compounds or by elementary sulphur; minute quantities of even insoluble sulphides, *e.g.*, in minerals, can readily be detected. Arsenides, selenides, antimonides, and tellurides do not respond.[28] On the basis of this reaction it is stated that fusion of selenium and sulphur produces a true sulphide. The presence of the pentathionate ion may be detected in the presence of sulphite by the appearance of an opalescence within 3 minutes when the solution is rendered slightly alkaline in the presence of formaldehyde.[29]

Hydroxylamine may be detected by means of the coloration with *p*-bromonitrosobenzene and α-naphthol.[30] Extensive tables have been drawn up showing the colour changes produced in dyes by further diazotisation and coupling; those substances best suited for the detection of nitrites are enumerated.[31]

Some microchemical reactions of various halogen acids have been described.[32] Phosphates may be detected in the presence of arsenates by the development of a blue coloration, either on filter paper or in a test-tube, on treatment with nitric acid–molybdate solution, benzidine, and ammonia.[33]

Quantitative.—From mathematical considerations of the theory of probability, the relation between the minimum weight of a sample to be taken for analysis and the degree of fineness of a heterogeneous mixture has been deduced,[34] whilst the extent to which results may be influenced by inaccuracies in measurement and observation has been considered for typical methods of chemical analysis.[35] The merits of adipic acid and of oxalic acid dihydrate as analytical standards have been discussed.[36] Metallic calcium of known purity can be weighed directly and dissolved in sucrose solution to afford a carbonate-free standard alkali solution.[37] The change of titre of thiosulphate solutions is attributed to the action of bacteria, of which there are three active kinds.[38] The protective action of alkali is ascribed to the restraining effect of alkalis on bacterial growths, which is greatest at p_{H} 9—10. Complete sterility is produced by the addition of 1% (by vol.) of amyl alcohol.

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[28] F. Feigl, *Z. anal. Chem.*, 1928, **74**, 369; **A.**, 1106.

[29] A. Czernotzky, *Z. anorg. Chem.*, 1928, **175**, 402; **A.**, 1204.

[30] J. Blom, *Biochem. Z.*, 1928, **194**, 385; **A.**, 674.

[31] J. V. Dubský and A. Okáč, *Publ. Fac. Sci. Univ. Masaryk*, 1927, No. 83, 1; **A.**, 1927, 1160; *Z. anal. Chem.*, 1928, **75**, 92.

[32] E. M. Chamot and C. W. Mason, *Mikrochem.*, 1928, **6**, 82; **A.**, 978.

[33] F. Feigl (with P. Krumholz), *Z. anal. Chem.*, 1928, **74**, 386; **A.**, 1107.

[34] J. Mika, *ibid.*, 1928, **73**, 257; **A.**, 496.

[35] F. Goudriaan, *Chem. Weekblad*, 1928, **25**, 52; **A.**, 262; B. D. Hartong, *ibid.*, p. 105; **A.**, 382.

[36] F. T. van Voorst, *ibid.*, p. 22; N. Schoorl, *ibid.*, p. 73; W. P. Jorissen, *ibid.*, p. 90; **A.**, 1928, 262.

[37] A. C. Shead, *J. Amer. Chem. Soc.*, 1928, **50**, 415; **A.**, 385.

The use of methyl-orange as indicator for the determination of the free acidity of solutions containing sulphates of zinc, copper, manganese, cadmium, or nickel gives results agreeing with those obtained potentiometrically.[39] Errors in the titration of acids and bases can frequently be greatly reduced by carrying out the operation in a non-aqueous medium such as acetone or 90% alcohol.[40] A table is set out correlating the various methods of expressing the acidity of solutions.[41]

An accurate method of ascertaining the p_{H} value of distilled water is the colorimetric, with a diluted neutralised solution of methyl-red; the quinhydrone-electrode method always involves an error on the acid side, which, however, diminishes with suitable buffering.[42] A critical study of the various methods of preparing and adjusting certain indicator solutions is described, and it is recommended that the p_{H} value of the indicator should be adjusted to a point midway between the extremes for the particular indicator.[43] A series of 25 mixed indicators, with their colour changes at p_{H} ranging from 3·25 to 10·8 has been compiled.[44] Data are supplied for determining p_{H} values between 6·7 and 10·0 with the aid of fast-green FCF.[45] A series of indicator papers which become grey at definite p_{H} values, but assume positive colours at values above or below the grey value, has been devised, covering the p_{H} range 1·5—8·0.[46] The divanillylidene*cyclo*hexanones are excellent indicators, as sensitive as methyl-red; the colour change occurs from p_{H} 7·8 to 9·4, that from 8 to 9 being so delicate as to be available for measuring p_{H} in this interval.[47] The speed with which the blue colour is developed by the reaction of malononitrile with α-naphthaquinone increases with increasing p_{H} value between the limits 2·5 and 11·5; small differences in the hydrogen-ion concentration of solutions may be detected by this test.[48] For solutions

[38] C. Mayr and E. Kerschbaum, *Z. anal. Chem.*, 1928, **73**, 321; **A.**, 607.

[39] E. Müller and F. Müller, *ibid.*, p. 47; **A.**, 386.

[40] K. Linderstrøm-Lang, *Dansk Tidsskr. Farm.*, 1928, **2**, 201; **A.**, 977.

[41] A. J. J. Vande Velde, *Natuurwetensch. Tijds.*, 1928, **10**, 145; **A.**, 1203.

[42] C. van der Hoeven, *Collegium*, 1928, 440; **A.**, 1203.

[43] W. H. Pierre and J. F. Fudge, *J. Amer. Chem. Soc.*, 1928, **50**, 1254; **A.**, 723.

[44] I. M. Kolthoff, *Biochem. Z.*, 1927, **189**, 26; **A.**, 1927, 1159.

[45] W. C. Holmes and E. F. Snyder, *J. Amer. Chem. Soc.*, 1928, **50**, 1907; **A.**, 976.

[46] W. U. Behrens, *Z. anal. Chem.*, 1928, **73**, 129; **A.**, 496.

[47] B. Samdahl, *J. Pharm. Chim.*, 1928, (viii), **7**, 162; **A.**, 523.

[48] W. Kesting, *Z. angew. Chem.*, 1928, **41**, 358; **A.**, 606.

of relatively low p_H value, benzoquinone gives a more delicate colour change, while β-naphthaquinone is used at the other extreme. The behaviour of various indicators in certain titrations has been examined,[49] and a study has been made, mainly from the academic side, of a number of azo-indicators.[50] Determination of the p_H of certain natural waters appears to be one of the best means of ascertaining the age of the water, since, on exposure, a gradual change to alkalinity occurs, beginning in the upper portion of the liquid.[51] Some buffer solutions for the alkaline range are described,[52] and also some electrodes for p_H determinations.[53]

Investigation of the applicability of iodometry to micro-analysis shows that in the reaction occurring in solutions about 0·001*N* with respect to iodate and containing excess of iodide and acid, the theoretical quantity of iodine is liberated and a satisfactory end-point subsequently obtained only when the product of the concentrations of iodide and acid lies between certain limits. Various other reactions have also been examined.[54]

Precipitation with " cupferron " from solutions containing free hydrochloric or nitric acid not exceeding *N*/1 affords a rapid means for the complete separation of bismuth from cadmium, lead, zinc, arsenic, silver, and quinquevalent antimony.[55] Two volumetric methods of determining bismuth depending on precipitation of the metal either by aluminium or by copper are described. In one case the cuprous chloride formed is titrated with potassium bromate, whilst in the other the metal is dissolved in acid ferric chloride solution, the ferrous chloride formed giving the measure of the bismuth.[56] A gravimetric process for micro-determination of bismuth as the oxy-iodide is described; alternatively, the dried precipitate may be heated in a current of air or oxygen and the liberated iodine collected in potassium iodide and titrated with thiosulphate.[57] The former process has also been modified for use with larger quantities of bismuth; [58] in the presence of much lead, a preliminary separation of bismuth as basic bismuth formate is made.

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[49] R. T. Thomson, *Analyst*, 1928, **53**, 315; **A.**, 857.

[50] A. Thiel and O. Peter, *Z. anorg. Chem.*, 1928, **173**, 169; **A.**, 977.

[51] G. Banchi, *Giorn. Chim. Ind. Appl.*, 1927, **9**, 518; **A.**, 1928, 262.

[52] I. M. Kolthoff and J. J. Vleeschhouwer, *Biochem. Z.*, 1927, **189**, 191; *Chem. Weekblad*, 1927, **24**, 526; **A.**, 1927, 1159.

[53] A. J. de la Cruz, *Philippine Agric.*, 1927, **16**, 307; **A.**, 1928, 607; F. Grossman, *Rocz. Chem.*, 1927, **7**, 567; **A.**, 1928, 607; E. Biilmann, A. Klit, and T. Swaetichin, *Biochem. J.*, 1928, **22**, 845; **A.**, 857.

[54] P. Putzeys, *Ann. Soc. Sci. Bruxelles*, 1927, **47**, *B*, i, 159; **A.**, 1928, 144.

[55] A. Pinkus and J. Dernies, *Bull. Soc. chim. Belg.*, 1928, **37**, 267; **A.**, 1109.

[56] H. Kubina and J. Plichta, *Z. anal. Chem.*, 1927, **72**, 201; **A.**, 1928, 39.

[57] R. Strebinger and W. Zins, *Mikrochem.*, 1927, **5**, 166; **A.**, 1928, 39.

[58] *Idem, Z. anal. Chem.*, 1927, **72**, 417; **A.**, 1928, 388.

The amount of chloride present in cadmium sulphide precipitated from hydrochloric acid solution depends on the acid concentration and the pressure at which precipitation is made.[59] The phenomenon is one of adsorption and is not due to the formation of a double salt. Cadmium can be rapidly determined by appropriate treatment of the precipitate given by pyridine and thiocyanate, whereby the compound is weighed as such;[60] lead is precipitated by these reagents as basic thiocyanate, which may be dealt with in a similar manner.[61] The blue coloration given by lead peroxide with a solution in acetic acid of tetramethyldiaminodiphenylmethane has again been applied to the detection and determination of lead;[62] iron and other impurities reduce the accuracy of the method.

A study has been made of the gravimetric determination of copper by the thiocyanate method, which may be applied in the presence of cobalt, nickel, zinc, manganese, arsenic, and iron, and, if tartaric acid be added, of antimony, bismuth, and tin.[63] Sulphides, *e.g.*, of mercury, nickel, and cobalt, soluble only with difficulty in dilute acids are readily attacked in the presence of hydrogen peroxide.[64] The end-point of the reaction between mercurous nitrate and potassium bromide may be ascertained by Fajans's method, sodium alizarinsulphonate being added as the indicator.[65] Modifications in methods of determining minute quantities of mercury are described.[66]

Gentle heating of the stannates of sodium and barium in a current of hydrogen chloride results in quantitative volatilisation of the tin as tetrachloride.[67] "Chloramine" may be used instead of iodine in the titration of stannous chloride provided that the acidity of the solution does not exceed 5%.[68] In solutions containing hydrochloric acid, the reduction of quinquevalent arsenic by hydrazine in presence of potassium bromide is quantitative only when the concentration of acid is high.[69] The Gutzeit method for the determination of arsenic has been the subject of a number of papers,[70] as also has the titration of arsenious acid with permanganate.[71] Small amounts of arsenic, after conversion into nearly neutral arsenate, are determined nephelometrically with a reagent containing cocaine and molybdic acid.[72]

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[59] H. B. Weiser and E. J. Durham, *J. Physical Chem.*, 1928, **32**, 1061; **A.**, 944.

[60] G. Spacu and J. Dick, *Z. anal. Chem.*, 1928, **73**, 279; **A.**, 499.

[61] *Idem*, *ibid.*, 1927, **72**, 289; **A.**, 1928, 264.

[62] A. D. Petrov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 311; **A.**, 726.

[63] I. M. Kolthoff and G. H. P. v. d. Meene, *Z. anal. Chem.*, 1927, **72**, 337; **A.**, 1928, 265.

[64] A. S. Komarovsky, *ibid.*, p. 293; **A.**, 1928, 265.

[65] R. Burstein, *Z. anorg. Chem.*, 1928, 325; **A.**, 265.

[66] A. Stock and W. Zimmermann, *Z. angew. Chem.*, 1928, **41**, 546; **A.**, 726; N. E. Schreiber, T. Sollmann, and H. S. Booth, *J. Amer. Chem. Soc.*, 1928, **50**, 1620; **A.**, 860.

[67] G. Jander and F. Busch, *Ber.*, 1927, **60**, [*B*], 2594; **A.**, 1928, 146.

[68] E. Rupp, *Z. anal. Chem.*, 1928, **73**, 51; **A.**, 387.

[69] H. Kubina and J. Plichta, *ibid.*, **74**, 235; **A.**, 1928, 972.

In sufficiently acid solutions, quinquevalent arsenic and antimony are completely reduced by hydriodic acid to the tervalent state, but the liberated iodine cannot be directly titrated in air; the method of utilising this reaction for quantitative work is described.[73] From a faintly ammoniacal solution of arsenate and antimonate containing fluoride, silver nitrate quantitatively precipitates the arsenate, free from antimony.[74] In a scheme for the quantitative separation of arsenic, antimony, and tin, the neutralised solution of the thio-salts, as usually obtained, is oxidised with hydrogen peroxide; hydrogen sulphide now precipitates from weakly acid solution only tin and antimony.[75] Ceric sulphate solution has been applied to the volumetric determination of antimony in the presence of arsenic, which may then be titrated with bromate.[76] The application of membrane methods of filtration in the determination of antimony as tetroxide has been studied,[77] and also a colorimetric process for small quantities, following, if necessary, a separation from tin by deposition on copper.[78]

Aluminium hydroxide, precipitated by warming a solution of an aluminium salt with potassium cyanate, is obtained in a less gelatinous condition than usual, becoming granular on subsequent boiling.[79] The colorimetric determination of aluminium with various reagents has been investigated—sodium alizarinsulphonate,[80] ammonium aurintricarboxylate,[81] and 1 : 2 : 5 : 8-tetrahydroxyanthraquinone.[82] Iron and aluminium phosphates are precipitated at p_H 5·0—5·4, whilst calcium phosphate is not precipitated below p_H 6·5. This separation is effected practically by adding an excess of ammonium acetate to the solution, slightly acid to thymol-blue.[83] Considerable occlusion of chromate occurs when aluminium and iron are precipitated as hydroxides from solutions containing chromate, although no chromate is occluded when these metals are precipitated as phosphates.[84] In the presence of sulphates, aluminium and nickel may be separated by the use of fusible white precipitate.[85] The oxide content of aluminium alloys can be determined by volatilisation at 275°, in a current of dry hydrogen chloride.[86] A volumetric process for determining aluminium depends on the formation of the complex oxalate $Al(C_2O_4)_3K_3$ which is neutral to methyl-red.[87]

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[70] H. Heidenhain, *J. Assoc. Off. Agric. Chem.*, 1928, **11**, 107; **A.**, 384; A. F. Lerrigo, *Analyst*, 1928, **53**, 90; **A.**, 263; C. H. Cribb, *ibid.*, 1927, **52**, 701; **B.**, 1928, 89; J. White, *ibid.*, p. 700; **B.**, 1928, 89; J. R. Stubbs, *ibid.*, p. 699; **B.**, 1928, 89; A. S. Dodd, *ibid.*, 1928, **53**, 152; **A.**, 498.

[71] N. Kanô, *Sci. Rep. Tôhoku Imp. Univ.*, 1927, **16**, 873; **A.**, 1928, 264; F. G. Germuth, *Amer. J. Pharm.*, 1927, **99**, 751; **A.**, 1928, 263.

[72] H. Kleinmann, *Deut. Z. ges. gerichtl. Med.*, 1927, **11**, 61; **A.**, 1928, 858.

[73] P. E. Winkler, *Helv. Chim. Acta*, 1927, **10**, 837; *Bull. Soc. chim. Belg.*, 1927, **36**, 491; **A.**, 1927, 1160; K. Pedersen-Bjergaard, *Dansk Tidsskr. Farm.*, 1928, **2**, 1; **A.**, 144.

[74] L. W. McCay, *J. Amer. Chem. Soc.*, 1928, **50**, 368; **A.**, 384.

[75] A. Thürmer, *Z. anal. Chem.*, 1928, **73**, 196; **A.**, 498.

[76] H. Rathsburg, *Ber.*, 1928, **61**, [*B*], 1663; **A.**, 1207.

[77] A. Simon and W. Neth, *Z. anal. Chem.*, 1927, **72**, 307; **A.**, 1928, 265.

[78] S. G. Clarke, *Analyst*, 1928, **53**, 373; **A.**, 983.

[79] R. Ripan, *Bul. Soc. Stiinte Cluj*, 1927, **3**, 311; **A.**, 1928, 499.

[80] J. H. Yoe and W. L. Hill, *J. Amer. Chem. Soc.*, 1928, **50**, 748; **A.**, 500.

[81] *Idem*, *ibid.*, 1927, **49**, 2395; **A.**, 1927, 1161.

Improvements have been made in the determination of ferrous iron in silicate rocks by means of hydrofluoric and sulphuric acids, hard-glass vessels being used.[88] The usual iodate procedure has been applied to the titration of ferrous iron.[89] Iron, aluminium, chromium, and titanium are precipitated as hydroxides from boiling solutions of their salts by hexamethylenetetramine in the presence of ammonium salts. Manganese, zinc, cobalt, and nickel are not precipitated under these conditions, thus permitting a separation of iron from these metals. Chromium, however, cannot be separated by this means.[90] The fading caused by the presence of phosphates in the colorimetric determination of titanium by means of hydrogen peroxide may be prevented by the addition of uranium acetate solution under certain conditions.[91] Knop's method for titrating iron is applied to micro-analysis, a 0·004*N*-dichromate solution being used; the same end-point is obtained potentiometrically and by using diphenylamine as an internal indicator.[92]

A method for the micro-determination of zinc is outlined, wherein the excess of ferrocyanide is determined by observation of the time required for the development of the blue colour when 0·05 mg.

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[82] I. M. Kolthoff, *J. Amer. Pharm. Assoc.*, 1928, **17**, 360; **A.**, 608.

[83] A. J. Patten and O. B. Winter, *J. Assoc. Off. Agric. Chem.*, 1928, **11**, 202; **A.**, 727.

[84] K. K. Järvinen, *Z. anal. Chem.*, 1928, **75**, 1; **A.**, 1206.

[85] B. Solaja, *Arhiv Hemiju Farm.*, 1928, **2**, 136; **A.**, 860.

[86] G. Jander and W. Brösse, *Z. angew. Chem.*, 1928, **41**, 702; **A.**, 860.

[87] A. Wöhlk, *Dansk Tidsskr. Farm.*, 1927, **1**, 525; **A.**, 1928, **38**; compare F. Feigl and G. Krauss, *Ber.*, 1925, **58**, [*B*], 398; *A.*, 1925, ii, 329.

[88] B. A. Soule, *J. Amer. Chem. Soc.*, 1928, **50**, 1691; **A.**, 861.

[89] G. B. Heisig, *ibid.*, p. 1687; **A.**, 1928, 861.

[90] P. Rây and A. K. Chattopadhya, *Z. anorg. Chem.*, 1928, **169**, 99; **A.**, 387.

[91] F. G. Germuth, *J. Amer. Chem. Soc.*, 1928, **50**, 1910; **A.**, 982.

[92] A. Benedetti-Pichler, *Z. anal. Chem.*, 1928, **73**, 200; **A.**, 500.

of iron is added to 5 c.c. of the supernatant liquid.[93] The use of stock ammonium sulphide solution, even freshly prepared, is deprecated on account either of partial precipitation of alkaline-earth metals or of formation of colloidal nickel sulphide. These difficulties are avoided by the passage of hydrogen sulphide into an ammoniacal solution.[94] For the quantitative precipitation of manganese by means of thiocyanate and pyridine, a large excess of pyridine is needed; the complex, $Mn(SCN)_2,4C_5H_5N$, may be weighed as such.[95] The analogous zinc complex may be treated similarly.[96] By using nitric acid (*d* 1·332) and carrying out the precipitation with potassium chlorate on a water-bath, manganese in any concentration can be determined accurately.[97]

A scheme for the separation, qualitative or quantitative, of calcium, barium, and strontium involves the removal of calcium first as the double potassium ferrocyanide, barium being then precipitated as chromate in the usual manner.[98] In a micro-chemical method for the determination of calcium, this metal is precipitated in presence of 4 vols. of alcohol as the hydrated sulphate and weighed in this form.[99] The permanganate method for calcium and the chromate method for barium have been applied on the micro-scale; in the latter case it is necessary to determine the excess of chromate added.[1] Silver and barium chromates form solid solutions with each other so that it is impossible to precipitate them successively by means of chromates; an approximate successive precipitation, however, occurs in 45% alcohol.[2] Calcium oxide, obtained by ignition of the oxalate at 1000° in an electric muffle, is cooled best in a desiccator over well-burnt lime.[3]

The pyrophosphate method for the determination of magnesium continues to attract attention;[4] a second precipitation under specified conditions is essential and a third may be necessary.[5]

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[93] R. Nakaseko, *Mem. Coll. Sci. Kyōtō*, 1928, *A*, **11**, 95; **A.**, 725.

[94] J. Röll, *Z. anal. Chem.*, 1927, **72**, 298; **A.**, 1928, 263.

[95] G. Spacu and J. Dick, *ibid.*, 1928, **74**, 188; **A.**, 982.

[96] *Idem*, *ibid.*, **73**, 356; **A.**, 1928, 608.

[97] M. Marqueyrol and L. Toquet, *Ann. Chim. anal.*, 1927, (ii), **9**, 289, 324; **A.**, 1927, 1162; 1928, 38.

[98] O. Macchia, *Notiz. chim.-ind.*, 1927, **2**, 311; **A.**, 1928, 385; *Chem.-Ztg.*, 1928, **52**, 281; **A.**, 498.

[99] F. Rogozinski, *Rocz. Chem.*, 1928, **8**, 275; **A.**, 1108; *Bull. Soc. chim.*, 1928, (iv), **43**, 464; **A.**, 980.

[1] W. Geilmann and R. Höltje, *Z. anorg. Chem.*, 1927, **167**, 128; **A.**, 1927, 1159.

[2] A. Mazzucchelli and B. Romani, *Gazzetta*, 1927, **57**, 900; **A.**, 1928, 264.

[3] A. Franke and R. Dworzak, *Z. anal. Chem.*, 1927, **72**, 129; **A.**, 1927, 1166.

[4] J. Majdel, *Arhiv Hemiju Farm.*, 1927, **1**, 216; **A.**, 1928, 38.

[5] (Miss) A. W. Epperson, *J. Amer. Chem. Soc.*, 1928, **50**, 321; **A.**, 386.

A rapid alkalimetric method for the determination of magnesium has been described[6] and also the use of tropæolin-OO in a colorimetric process.[7]

Uranyl zinc acetate may be used in the gravimetric determination of sodium in the absence of lithium, strontium, phosphate, and large amounts of oxalate and tartrate; [8] barium, calcium, magnesium, and zinc do not interfere. Subsequent treatment of the precipitate with ferrocyanide serves for the basis of a micromethod applicable to biological material.[9] Further work has also appeared on the use of the corresponding magnesium reagent.[10] Dihydroxytartaric acid can only be used for the quantitative determination of sodium by working at 0° and introducing a correction for the solubility of the sodium salt.[11] Various modifications of the cobaltinitrite process for potassium have been made; treatment of the washed precipitate with acid ferrous sulphate solution liberates nitric oxide which may be measured.[12] An iodometric process for treating the cobaltinitrite precipitate serves for micro-determination.[13] Modifications of the tartrate–cobaltinitrite method have been made to obtain stoicheiometric results.[14] Two other papers deal with the chloroplatinate [15] and the perchlorate process.[16]

The use of strontium chloride, admixed with ammonium chloride, has been studied for fusion with silicates in the determination of alkali metals therein.[17] 8-Hydroxyquinoline is used for the precipitation and determination of aluminium and magnesium in certain silicates; the reagent is also useful in removing these metals prior to alkali determination.[18]

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[6] L. Galimberti and E. Zoccheddu, *Ann. Chim. Appl.*, 1928, **18**, 286; **A.**, 980.

[7] J. Zahradníček, *Biochem. Z.*, 1927, **191**, 61; **A.**, 1928, 145.

[8] H. H. Barber and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1928, **50**, 1625; **A.**, 859.

[9] H. K. Barrenscheen and L. Messiner, *Biochem. Z.*, 1927, **189**, 308; **A.**, 1928, 96.

[10] E. di Benedetto and A. D. Marenzi, *Rev. Centr. Estud. Farm. Bioquim.*, 1927, **16**, 592; **A.**, 1928, 1205; A. Nau, *Bull. Soc. Pharm. Bordeaux*, 1927, **65**, 67; **A.**, 1928, 385; Weiland, *Mitt. Kali-Forsch.-Anst.*, 1927, 21; **A.**, 1928, 385.

[11] A. P. Okatov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 661; **A.**, 979.

[12] G. Jander and H. Faber, *Z. anorg. Chem.*, 1928, **173**, 225; **A.**, 980.

[13] A. Leulier, L. Velluz, and H. Griffon, *Bull. Soc. Chim. biol.*, 1928, **10**, 891; **A.**, 1205.

[14] M. Wikul, *Z. anal. Chem.*, 1927, **72**, 345; **A.**, 1928, 264; compare *Z. anorg. Chem.*, 1926, **151**, 338; **A.**, 1926, 491.

[15] M. McCurdy, *Proc. Nova Scotian Inst. Sci.*, 1927, **16**, 142; **A.**, 1928, 859.

[16] A. T. Dalsgaard, *Dansk Tidsskr. Farm.*, 1928, **2**, 257; **A.**, 1205.

[17] J. Kavina, *Chem. Listy*, 1928, **22**, 267; **A.**, 859.

[18] J. Robitschek, *Chem. Obzor.*, 1927, **2**, 325; *J. Amer. Ceram. Soc.*, 1928, **11**, 587; **B.**, 895.

Fusion with bismuth in place of lead usually effects a saving of time in the separation of iridium and rhodium.[19] The addition of potassium iodide to solutions of these two metals precipitates the rhodium as iodide.[20] Schemes for the analysis of iridium [21] and for separating the various platinum metals are described.[22] Platinum, palladium, and rhodium, but not osmium and ruthenium, form insoluble complex compounds on addition of thiocyanate; iridium gives an unsuitable precipitate.[23] The coloration given with potassium iodide may be utilised for rapid determination of palladium in platinum.[24] Osmium tetroxide is distilled from a chromic acid mixture, the sulphide being then precipitated and ignited to metal.[25]

Thorium is completely precipitated as subphosphate,

$$ThP_2O_6,11H_2O,$$

from boiling solutions containing 10% of hydrochloric acid; a subsequent precipitation as oxalate must be made, as conversion into pyrophosphate by ignition is not quantitative.[26] In the absence of mannitol, glycerol, or dextrose, only about 40% of germanic acid is neutralised by caustic soda, with phenolphthalein as indicator. The mannitol complex liberates iodine from iodide–iodate solution.[27] The important separation of iron from gallium may be effected by means of α-nitroso-β-naphthol; [28] aluminium and also ferric iron may be separated from beryllium by precipitation with 8-hydroxyquinoline in acetic acid solution.[29] The use of curcumin in colorimetric determination of beryllium has been described.[30] Conflicting views exist as to the value of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone for this purpose.[31] Precipitation of beryllium with ammonia gives low results; the use of ammonium nitrite is satisfactory if boiling is effected in presence of methyl alcohol in order to volatilise methyl nitrite. The pyrophosphate method is described and also a number of separations by means of tannic acid.[32] Further investigations of the analytical chemistry of tantalum, niobium, and their mineral associates are described.[33] Examination has been made of various gravimetric methods of determining molybdenum; conversion of the sulphide into trioxide is preferred.[34]

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[19] B. Karpov, *Ann. Inst. Platine*, 1928, **6**, 98; **A.**, 983.

[20] V. V. Lebedinski, *ibid.*, 1927, **5**, 364; **A.**, 1928, 728.

[21] O. E. Zvjagintsev, *ibid.*, p. 189; **A.**, 1928, 728.

[22] Anon., *Chem. Eng. Min. Rev.*, 1928, **20**, 142, 170; **A.**, 861.

[23] V. N. Ivanov, *Ann. Inst. Platine*, 1926, **4**, 331; **A.**, 1927, 1162.

[24] O. E. Zvjagintsev, *ibid.*, p. 364; **A.**, 1927, 1162.

[25] E. Fritzmann, *ibid.*, 1928, **6**, 116; *Z. anorg. Chem.*, 1928, **169**, 356; **A.**, 388.

[26] F. Hecht, *Z. anal. Chem.*, 1928, **75**, 28; **A.**, 1206.

[27] A. Tchakirian, *Compt. rend.*, 1928, **187**, 229; **A.**, 983.

[28] J. Papish and L. E. Hoag, *J. Amer. Chem. Soc.*, 1928, **50**, 2118; **A.**, 981.

[29] I. M. Kolthoff and E. B. Sandell, *ibid.*, p. 1900; **A.**, 981.

[30] I. M. Kolthoff, *ibid.*, p. 393; **A.**, 386.

[31] *Idem, ibid.*; H. Fischer, *Z. anal. Chem.*, 1928, **73**, 54; **A.**, 385.

[32] L. Moser and J. Singer, *Monatsh.*, 1927, **48**, 673; **A.**, 1928, 145.

Tungstic acid may be separated from a freshly precipitated mixture with metastannic acid or from a mixture with silica dehydrated at 130° by treatment with sodium tungstate solution under suitable conditions.[35] Volatilisation in hydrogen chloride has been applied to the analysis of sodium and barium tungstates.[36] A somewhat arbitrary iodometric method for the determination of small quantities of thallium has been worked out.[37]

On account of the readiness with which dry hydrazine hydrogen selenate explodes in contact with hydrogen chloride vapour, selenates should be reduced to selenites by hydrochloric acid before hydrazine hydrate is added to complete the reduction.[38] The reduction of selenious acid by hydriodic acid for analytical purposes is best effected in presence of carbon disulphide; otherwise part of the iodine liberated is adsorbed in the precipitated selenium.[39]

When iodine is run into sulphite solution low results occur and these are attributed less to oxidation than to volatilisation which is rendered easier by the increasing acidity due to the hydriodic acid formed. A study has also been made of the oxidation of sulphites by air, having in view the possibilities of losses in analytical processes for determining sulphurous acid involving distillation.[40] The high results obtained when barium sulphate is precipitated in presence of chromate can be diminished by reduction of the chromate, but it is preferable that all the chromium should be removed first.[41] The conditions under which the precipitation of sulphuric acid as barium sulphate takes place from solutions containing antimony, tartaric acid, and hydrochloric acid (*e.g.*, in the analysis of antimony sulphide) have been investigated with the view of obtaining reproducible results, independent of the concentration of antimony and with minimal corrections.[42]

A series of tests has been carried out to check the solubility of barium sulphate in various concentrations of acid; the results point to the need for systematic investigation of all the conditions for the determination of very small amounts of sulphate.[43] If concentrated solutions of sulphate are treated with concentrated barium chloride solution, and the liquid is then diluted and heated for some time, barium sulphate may be obtained in a coarse granular form which does not adsorb other salts from the solution.[44] Some observations have been made on the sources of error of the benzidine method for the determination of sulphates,[45] whilst a colorimetric micro-method is based on a preliminary precipitation of benzidine sulphate.[46] In the direct iodometric determination of persulphate, potassium chloride[47] and ammonium chloride act as accelerators of the reaction;[48] some indirect methods are also described.[48] All polythionates, except dithionate, are oxidised completely to sulphate by heating with iodine in bicarbonate solution under appropriate conditions. Trithionates are oxidised at the boiling temperature by copper sulphate; tetrathionate, thiosulphate, and sulphite, but not pentathionate, interfere.[49]

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[33] W. R. Schoeller and A. R. Powell, *Analyst*, 1928, **53**, 258; **A.**, 608; W. R. Schoeller and E. F. Waterhouse, *ibid.*, pp. 467, 515; **A.**, 1207; I. Wada and S. Kato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1927, **6**, 227; **A.**, 1927, 1162.

[34] E. Wendehorst, *Z. anal. Chem.*, 1928, **73**, 453; **A.**, 861.

[35] J. Ciochina, *ibid.*, **72**, 429; **A.**, 387.

[36] G. Jander and D. Mojert, *Z. anorg. Chem.*, 1928, **175**, 270; **A.**, 1206.

[37] J. Proszt, *Z. anal. Chem.*, 1928, **73**, 401; **A.**, 726.

[38] J. Meyer and W. Aulich, *Ber.*, 1928, **61**, [*B*], 1839; **A.**, 1200.

[39] R. Berg and M. Teitelbaum, *Chem.-Ztg.*, 1928, **52**, 142; **A.**, 383.

[40] H. M. Mason and G. Walsh, *Analyst*, 1928, **53**, 142; **A.**, 497.

[41] M. N. Pavlov, *Ukraine Chem. J.*, 1926, **2**, 353; **A.**, 1927, 1160.

[42] S. von Finály, *Z. anal. Chem.*, 1928, **75**, 17; **A.**, 1204.

The microchemical determination of phosphoric acid as strychnine phosphomolybdate has been investigated;[50] when washed with 10% nitric acid, the precipitate has a composition corresponding with the formula $11MoO_3,H_3PO_4,(Str)_3,2HNO_3$.[51] The orange colour given by sodium salicylate with uranyl acetate is utilised for the volumetric determination of phosphate.[52] Zinc and cadmium amalgams reduce sexavalent molybdenum quantitatively to the tervalent state, and this reduction has been applied to the determination of phosphates, following precipitation as ammonium phosphomolybdate.[53] This compound can be titrated directly in ammoniacal solution in the presence of acetone.[54] The statement[55] that the blue coloration obtained in the usual Denigès colorimetric process[56] is quantitatively discharged by chlorine water is challenged.[57] The methods of precipitating magnesium ammonium phosphate in the presence and absence of ammonium acetate have been compared;[58] in the absence of molybdate ions, the acetate method more readily produces a crystalline precipitate. Conditions for the iodometric determination of phosphites are described.[59]

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[43] H. R. Jensen, *Analyst*, 1928, **53**, 136; **A.**, 497.

[44] V. Njegovan and V. Marjanović, *Z. anal. Chem.*, 1928, **73**, 271; **74**, 191; **A.**, 497, 978.

[45] O. Nydegger, *Chem.-Ztg.*, 1928, **52**, 318; **A.**, 607.

[46] J. Yamazaki, *Bull. Chem. Soc. Japan*, 1928, **3**, 173; **A.**, 1107.

[47] L. von Zombory, *Z. anal. Chem.*, 1928, **73**, 217; **A.**, 497.

[48] A. Schwicker, *ibid.*, **74**, 433; **A.**, 1928, 1107.

[49] E. H. Riesenfeld and G. Sydow, *Z. anorg. Chem.*, 1928, **175**, 74; **A.**, 1204.

[50] C. Antoniani and R. B. Jona, *Giorn. Chim. Ind. Appl.*, 1928, **10**, 203; **A.**, 979.

[51] C. Antoniani, *ibid.*, p. 408; **A.**, 1265.

[52] L. Duparc and E. Rogovine, *Helv. Chim. Acta*, 1928, **11**, 598; **A.**, 979.

[53] K. Someya, *Z. anorg. Chem.*, 1928, **175**, 347; **A.**, 1204; S. Hakomori, *Sci. Rep. Tôhoku Imp. Univ.*, 1927, **16**, 719; **A.**, 1927, 1160.

[54] G. Hammarsten, *Compt. rend. Trav. Lab. Carlsberg*, 1928, **17**, No. 5, 1; **A.**, 263.

[55] V. V. Ciurea, *Bul. Soc. Chim. România*, 1927, **9**, 86; **A.**, 1928, 384.

With suitable precautions, nitrates may be determined by reduction to nitrites by ferrous sulphate in concentrated sulphuric acid solution, the end-point being shown by the coloration due to the compound of ferrous sulphate with nitric oxide; the effect of halogens and metals on the process is given.[60] Reaction between azides and iodine, induced by sulphides and thiosulphate (*vide supra*) is also promoted by carbon disulphide, especially when alcohol or acetone is present; a volumetric process for the iodometric determination of azides is based on this action.[61]

A discrepancy is recorded in the strength of the picric acid solution used as an artificial standard in a colorimetric process for determining silica.[62]

Small quantities of free chlorine, *e.g.*, in tap-water, may be determined colorimetrically with *as*-dimethyl-*p*-phenylenediamine, the water being brought to a definite acidity and the colour matched with standard solution of methyl-red;[63] the pink colour is also given by other mild oxidising agents, *e.g.*, iodine or ferric chloride. The addition of concentrated zinc sulphate solution greatly increases the sensitiveness of the methylene-blue perchlorate coloration; the colour given by chlorates must be neutralised by means of sodium nitrate.[64] For the purpose of determining perchlorate in presence of large amounts of chlorate, the latter may be reduced to chloride by means of sulphur dioxide; after removal of the excess of reducing agent, the perchlorate is determined by means of titanous chloride.[65] An indirect bromometric process for the determination of chlorates is described; [66] perchlorates are reduced by refluxing with titanic and cadmium sulphates in the presence of zinc and iron powders, the chlorides being then determined volumetrically.[67] Further work is recorded on the determination of minute quantities of iodine.[68] The use of membrane filters for determining fluorine as calcium fluoride is described; [69] the filtration is much more rapid in the presence of nitrate ions.

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[56] Compare G. Denigès, *Compt. rend.*, 1928, **186**, 318; **A.**, 263.

[57] I. Voicu, *Bul. Soc. Chim. România*, 1928, **10**, 50; **A.**, 979.

[58] W. M. McNabb, *J. Amer. Chem. Soc.*, 1928, **50**, 300; **A.**, 384.

[59] P. Carré, *Compt. rend.*, 1928, **186**, 436; **A.**, 384.

[60] L. Szebellédy, *Z. anal. Chem.*, 1928, **73**, 145; **74**, 232; **A.**, 498, 979.

[61] F. Feigl and E. Chargaff, *ibid.*, **74**, 376; **A.**, 1106.

[62] E. J. King and C. C. Lucas, *J. Amer. Chem. Soc.*, 1928, **50**, 2395; **A.**, 1205. Compare F. Diénert and F. Wandenbulcke, *Compt. rend.*, 1923, **176**, 1478; *A.*, 1923, ii, 507.

[63] K. Alfthan, *Finska Kemistamfundets Medd.*, 1927, **36**, 109; *J. Amer. Water Works Assoc.*, 1928, **20**, 409; **B.**, 838. Compare I. M. Kolthoff, *Chem. Weekblad*, 1926, **23**, 203; **B.**, 1926, 517.

[64] O. S. Fedorova, *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 509; **A.**, 1927, 1159.

Sources of error in the determination of carbonic acid by precipitation as barium carbonate and titration of the excess of alkali are pointed out.[70] A volumetric process for the determination of small amounts of carbonic acid and free ammonia present in distilled water is described, together with the corrections which must be applied.[71] The direct oxidation of cyanide by means of permanganate in strongly alkaline solution is greatly accelerated by the addition of copper sulphate; this process for determining alkali cyanides depends on immediate conversion of the permanganate into manganate.[72]

Organic Analysis.

Qualitative.—Some further mercury alkyl and aryl halides have been prepared for the purpose of identifying the halides.[73] The Grignard reagents from certain tertiary aliphatic halides give positive results in the colorimetric test previously described [74] provided that 5 minutes be allowed for the reaction with the Michler's ketone.[75] Small quantities of organo-magnesium halides may be rapidly identified by crystalline derivatives prepared from α-naphthylcarbimide.[76] Some colour and microchemical reactions of the following substances are described: mannitol,[77] atropine,[78] morphine,[79] cholesterol,[80] ergosterol,[81] hyoscyamine,[82] citric acid,[83] carbohydrates,[84] and volatile aldehydes and ketones, such as those present in fruits and essences.[85] Vanillin and piperonal behave like other aldehydes in giving sensitive colour reactions with certain alkaloids.[86] Some aldehydes give colour reactions with lecithin and sulphuric acid.[87] A sensitive differentiation of phthalic and terephthalic acids depends on the rate of precipitation of complex compounds with pyridine and copper or cobalt salts.[88] Methods for the micro-identification of the three xylenes in admixture are described.[89]

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[65] E. Spitalski and S. Jofa, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 75; *Z. anorg. Chem.*, 1928, **169**, 309; **A.**, 383.

[66] K. Peters and E. Deutschländer, *Apoth.-Ztg.*, 1926, **41**, 594; **A.**, 1928, 383.

[67] E. S. Tomula, *Ann. Acad. Sci. Fennicae*, 1927, *A*, **29**, No. 21; **A.**, 1928, 263.

[68] P. A. Meerburg, *Z. physikal. Chem.*, 1927, **130**, 105; **A.**, 1927, 1160; J. F. McClendon, *J. Amer. Chem. Soc.*, 1928, **50**, 1093; **A.**, 607; L. S. van der Vlugt, *Chem. Weekblad*, 1928, **25**, 196; **A.**, 497.

[69] G. G. Kandilarov, *Ber.*, 1928, **61**, [*B*], 1667; **A.**, 1204.

[70] J. Lindner, *Z. anal. Chem.*, 1927, **72**, 135; **A.**, 1927, 1161.

[71] N. Bjerrum, *Ann. Acad. Sci. Fennicae*, 1927, *A*, **29**, No. 1; **A.**, 1928, 264.

[72] H. Gall and G. Lehmann, *Ber.*, 1928, **61**, [*B*], 670; **A.**, 624.

[73] E. L. Hill, *J. Amer. Chem. Soc.*, 1928, **50**, 167; **A.**, 269.

[74] H. Gilman and F. Schulze, *ibid.*, 1925, **47**, 2002; *A.*, 1925, ii, 1011.

[75] *Idem*, *Bull. Soc. chim.*, 1927, (iv), **41**, 1479; **A.**, 1928, 160.

[76] H. Gilman and M. Furry, *J. Amer. Chem. Soc.*, 1928, **50**, 1214; **A.**, 660.

[77] L. Ekkert, *Pharm. Zentr.*, 1928, **68**, 433; **A.**, 1114.

[78] *Idem*, *ibid.*, **69**, 529; **A.**, 1145; M. Wagenaar, *Pharm. Weekblad*, 1928, **65**, 197; **A.**, 532.

Quantitative.—Oxidation with permanganic anhydride is applied to the determination of organic carbon in soil and in pure organic compounds.[90] The baryta method for determining carbon dioxide is applied to organic analysis, the excess of barium hydroxide being titrated and the precipitated barium carbonate being converted into and weighed as sulphate.[91] An apparatus for the determination of carbon and hydrogen without the use of catalysts is described, in which combustion takes place in a current of pure oxygen.[92] Some notes on the rapid determination of carbon and hydrogen in organic compounds are recorded.[93] Pregl's "universal filling" has been successfully applied on a macro-scale,[94] and various observations have been made with regard to micro-analytical methods for carbon and hydrogen.[95] By combustion in a closed apparatus with a measured volume of oxygen, the approximate oxygen content of organic compounds is obtained, the values being chiefly of service in helping to confirm the presence of this element.[96]

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[79] L. Ekkert, *Pharm. Zentr.*, 1928, **69**, 198; **A.**, 533; M. Wagenaar, *Pharm. Weekblad*, 1927, **64**, 1119; **A.**, 1927, 1210.

[80] L. Ekkert, *Pharm. Zentr.*, 1928, **69**, 97; **A.**, 410.

[81] *Idem*, *ibid.*, p. 276; **A.**, 1928, 1000.

[82] M. Wagenaar, *Pharm. Weekblad*, 1928, **65**, 549; **A.**, 1030.

[83] *Idem*, *ibid.*, 1927, **64**, 1135; **A.**, 1927, 1213.

[84] L. Ekkert, *Pharm. Zentr.*, 1928, **69**, 597; **A.**, 1220; S. Y. Wong, *Chinese J. Physiol.*, 1928, **2**, 255; **A.**, 1219.

[85] C. Griebel and F. Weiss, *Mikrochem.*, 1927, **5**, 146; **A.**, 1928, 82.

[86] L. van Itallie and A. J. Steenhauer, *Arch. Pharm.*, 1927, **265**, 696; **A.**, 1928, 311.

[87] D. Migliacci, *Boll. Chim. farm.*, 1928, **67**, 324; **A.**, 1043.

[88] R. Ripan, *Bul. Soc. Stiinte Cluj*, 1927, **3**, 308; **A.**, 1928, 1006.

[89] M. Magita, *Bull. Chem. Soc. Japan*, 1928, **3**, 191; **A.**, 1234.

[90] L. U. De Nardo, *Giorn. Chim. Ind. Appl.*, 1928, **10**, 253; **A.**, 909.

[91] P. Dickens, *Chem. Fabr.*, 1928, 293; **A.**, 784.

[92] I. Marek, *Arhiv Hemiju Farm.*, 1927, **1**, 188; *Bull. Soc. chim.*, 1928, (iv), **43**, 910; **A.**, 82.

[93] E. Berl, A. Schmidt, and K. Winnacker, *Ber.*, 1928, [*B*], 83; **A.**, 312.

[94] W. Davies, *J.*, 1927, 3161; **A.**, 1928, 190.

[95] H. D. K. Drew and C. R. Porter, *J. Soc. Chem. Ind.*, 1928, **47**, 17T; **A.**, 312; B. Bobrański and E. Sucharda, *Rocz. Chem.*, 1928, **8**, 290; **A.**, 1107; R. Goubau, *Natuurwetensch. Tijds.*, 1928, **10**, 129; **A.**, 1205.

Many amino-acids can be titrated in acetone solution with alcoholic hydrochloric acid, benzeneazo-α-naphthylamine being employed as indicator.[97] In Kjeldahl digestions, the ammonia, up to 20 mg. of nitrogen per 100 c.c., can be determined by direct Nesslerisation in presence of gum arabic.[98] A modified Dumas apparatus is described for the volumetric determination of carbon and nitrogen at the same time.[99] Possible sources of error in the micro-Dumas method are indicated.[1]

In a micro-analytical process for sulphur, the organic compound is volatilised from a platinum boat in a stream of hydrogen, the sulphur being then retained on freshly-reduced pure nickel as sulphide.[2] The addition of alkali chloride in the Carius method for sulphur is recommended for use with difficultly oxidisable substances.[3] Determinations of the effect of time and temperature on Pregl's micro-Carius method have been made with various types of compounds.[4] A volumetric process for determining selenium in halogen-free compounds is described.[5]

Treatment in alcoholic solution with sodium, followed by hydrogen peroxide, affords a method for determining halogens, especially suitable for naphthalene derivatives, terpenes, and heterocyclic compounds.[6] A modification of Stepanov's method has been made to allow the determination of halogens in the benzene nucleus.[7] To prevent loss of ammonium halide in ter Meulen's process for halogens, the exit gases are passed over strongly heated barium carbonate; in certain cases the use of a hydrogenating catalyst is necessary.[8]

Organo-lead compounds in which the metal is directly attached to aryl groups are analysed by oxidation by means of nitric–sulphuric acid.[9] The small loss of mercury that occurs when organic mercurials are so treated introduces a serious error in micro-analysis; good results are obtained by heating with fuming nitric acid in a sealed tube.[10]

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[96] G. G. Glockler and L. D. Roberts, *J. Amer. Chem. Soc.*, 1928, **50**, 828; **A.**, 536.

[97] K. Linderstrøm-Lang, *Z. physiol. Chem.*, 1928, **173**, 32; **A.**, 536; *Compt. rend. Trav. Lab. Carlsberg*, 1927, **17**, No. 4, 1; **A.**, 1928, 313.

[98] H. M. Chiles, *J. Amer. Chem. Soc.*, 1928, **50**, 217; **A.**, 312.

[99] R. Vandoni and M. Algrain, *Bull. Soc. chim.*, 1928, (iv), **43**, 255; **A.**, 436.

[1] F. Böck and K. Beaucourt, *Mikrochem.*, 1928, **6**, 69; **A.**, 978.

[2] S. Hanai, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, **7**, 915; **A.**, 1267; B. Kubota and S. Hanai, *Bull. Chem. Soc. Japan*, 1928, **3**, 168; **A.**, 1106.

[3] V. C. Rogers and G. Dougherty, *J. Amer. Chem. Soc.*, 1928, **50**, 1231; **A.**, 660.

[4] L. Bermejo y Vida, *Chim. et Ind.*, 1928, **20**, 221; **A.**, 1106.

[5] W. E. Bradt and R. E. Lyons, *Proc. Indiana Acad. Sci.*, 1926, **36**, 195; **A.**, 1928, 436.

[6] M. Proner, *Rocz. Farm.*, 1926, **4**, 99; **A.**, 1928, 436.

[7] G. Favrel and Bucher, *Ann. Chim. anal.*, 1927, (ii), **9**, 321; **A.**, 1928, 82.

[8] H. ter Meulen, *Rec. trav. chim.*, 1928, **47**, 698; **A.**, 724.

The ability of methylglyoxal to form iodoform is used as a basis for its determination.[11] The $-CH_2·OH$ group in ethylene chlorohydrin is completely oxidised to $>C{:}O$ by warming with diazobenzenesulphonic acid, and a colorimetric process is based on this reaction.[12] Volumetric methods of determining carbamide depend on the oxidation of the dixanthyl derivative by permanganate,[13] or by dichromate.[14] The tetrapropylammonium ion is quantitatively precipitated under specified conditions as the diamminochromithiocyanate.[15] Some investigations on the analysis of mixtures of ethyl alcohol, ethyl acetate, acetic acid, and water have been made.[16] The addition of a small proportion of acetyl chloride to the acetic anhydride before mixing with pyridine gives satisfactory results with primary alcohols and most secondary alcohols.[17] Some organic sulphides are quantitatively oxidised to sulphones by perbenzoic acid, the excess of oxidant being ascertained iodometrically.[18]

A series of amino-acids and dipeptides has been titrated with acid and alkali, thymol-blue and alizarin-yellow being used as indicators.[19] A method is described for the determination of phenylalanine by oxidation to benzoic acid (average conversion, 95·2%) by dichromate.[20] Tannic acid may be determined by precipitation at 40—50° with a measured excess of titanium chloride; interference of gallic, salicylic, mandelic, and other hydroxy-acids is avoided by working in solutions containing hydrochloric acid within certain limits.[21]

The formation of insoluble ferric salts by most sulphinic acids is utilised for determination both of the acids and of the ferric ion.[22] Sulphinic acids react quantitatively with iodide–iodate solution,

[9] H. Gilman and J. Robinson, *J. Amer. Chem. Soc.*, 1928, **50**, 1714; **A.**, 1041.

[10] A. Verdino, *Mikrochem.*, 1928, **6**, 5; **A.**, 386.

[11] F. Fischler and R. Boettner, *Z. anal. Chem.*, 1928, **74**, 28; **A.**, 870.

[12] M. B. Sapadinski, *ibid.*, 273; *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 695; **A.**, 989.

[13] J. M. Luck, *J. Biol. Chem.*, 1928, **79**, 211; **A.**, 1229.

[14] H. Cordebard, *Bull. Soc. Chim. biol.*, 1928, **10**, 461; **A.**, 661.

[15] F. Hein and F. A. Segitz, *Z. anal. Chem.*, 1927, **72**, 119; **A.**, 1927, 1175.

[16] S. Poznanski, *J. Amer. Chem. Soc.*, 1928, **50**, 981; *Rocz. Chem.*, 1928, **8**, 152, 229, 263, 272; **A.**, 784.

[17] A. Verley, *Bull. Soc. chim.*, 1928, (iv), **43**, 469; **A.**, 615.

[18] L. N. Lewin, *J. pr. Chem.*, 1928, (ii), **118**, 282; **A.**, 505.

[19] K. Felix and H. Müller, *Z. physiol. Chem.*, 1927, **171**, 4; **A.**, 1928, 535.

[20] G. Kollmann, *Biochem. Z.*, 1928, **194**, 1; **A.**, 660.

[21] S. Krishna and N. Ram, *Ber.*, 1928, **61**, [*B*], 771; **A.**, 660.

[22] S. Krishna and H. Singh, *J. Amer. Chem. Soc.*, 1928, **50**, 792; **A.**, 536.

no elimination of the acid group occurring in the nineteen cases examined.[23]

Dextrose and other reducing sugars may be rapidly and accurately titrated with potassium ferricyanide, picric acid being used as indicator; the procedure employed varies according as the sugar content is relatively large or small.[24] A detailed study of the oxidation of dextrose by alkaline copper solutions has been made.[25]

Methods for the quantitative separation and determination of strychnine and brucine by means of the hydroferrocyanide are described.[26] Strychnine silicotungstate is shown to possess no simple molecular constitution, although its composition is constant: the ratio ash : alkaloid is found to be 0·422.[27]

For gravimetric determination of vanillin, precipitation with *m*-nitrobenzhydrazide is recommended.[28] Koppeschaar's bromination method for phenols and amines is, where applicable, more satisfactory than direct titration with bromate.[29] The coloration given by ferric chloride with a number of *o*-dihydroxybenzene derivatives is applied to their determination.[30] The intense red and blue colorations given by 2 : 6- and 2 : 4-dinitrotoluene, respectively, with alcoholic sodium hydroxide are applied to the determination of nitrotoluenes in nitrobenzene.[31] The amino-nitrogen in nitrotoluidines, their acetyl derivatives, and in nitroarsanilic acid is quantitatively obtained as ammonia by refluxing with sodium hydroxide solution.[32] Some notes on the determination of small quantities of benzoic, cinnamic, and salicylic acid are recorded.[33]

Physical Methods.

Further work is recorded on the use of the centrifuge in volumetric micro-analysis;[34] details are given for the sulphate–barium[35] and for the chromate–lead[36] precipitations. The volume of the precipitate, after centrifuging, may be measured in the case of sulphate, calcium, magnesium, phosphate, and potassium ions; in the first case, the quantity must be not less than 4 mg.[37] The opacity of fine precipitates may be prevented from changing appreciably with time by addition of dextrin or gum arabic.[38] Further extensions have been made in radiometric microanalysis.[39]

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[23] S. Krishna and B. Das, *J. Indian Chem. Soc.*, 1927, **4**, 367; **A.**, 1928, 82.

[24] A. Ionesco-Matiu, *Bul. Soc. Chim. România*, 1927, **9**, 68; **A.**, 1928, 398.

[25] C. A. Amick, *J. Physical Chem.*, 1927, **31**, 1441; **A.**, 1927, 1213.

[26] M. Gadreau, *J. Pharm. Chim.*, 1927, (viii), **6**, 145; **A.**, 1928, 314. Compare H. I. Cole, *Philippine J. Sci.*, 1923, **23**, 97; *A.*, 1923, ii, 703; and W. M. Cumming and D. G. Brown, *J. Soc. Chem. Ind.*, 1928, **47**, 84T.

[27] E. Stuber and B. Kljatschkina, *Arch. Pharm.*, 1928, **266**, 33; **A.**, 532.

[28] J. Pritzker and R. Jungkunz, *Chem.-Ztg.*, 1928, **52**, 537; **A.**, 1009.

[29] A. R. Day and W. T. Taggart, *Ind. Eng. Chem.*, 1928, **20**, 545; **A.**, 660.

[30] H. Schmalfuss, K. Spitzer, and H. Brandes, *Biochem. Z.*, 1927, **189**, 226; **A.**, 1927, 1213.

[31] H. Muraour, *Bull. Soc. chim.*, 1928, (iv), **43**, 71; **A.**, 279.

[32] N. Semiganovsky, *Z. anal. Chem.*, 1927, **72**, 295; **A.**, 1928, 314. See *ibid.*, p. 27; **A.**, 1927, 1062.

[33] J. R. Nicholls, *Analyst*, 1928, **53**, 19; **A.**, 313.

[34] R. F. Le Guyon, *Ann. Chim.*, 1928, (x), **10**, 50; **A.**, 1105.

[35] *Idem*, *Bull. Soc. chim.*, 1927, (iv), **41**, 1387; **A.**, 1928, 36; A. Gunder, *Z. anal. Chem.*, 1928, **73**, 441; **A.**, 857.

[36] R. F. Le Guyon and R. F. Auriol, *Compt. rend.*, 1928, **186**, 1551; **A.**, 860.

The presence, in alcohol, of less than 0·001% of benzene can be determined spectroscopically.[40] The application of a polarisation spectrophotometer to colorimetric [41] and nephelometric analysis [42] has been investigated, and the photoelectric spectrophotometric method, as developed by von Halban, has been extended to the micro-determination of iron and titanium.[43] A spectral method is described by which as little as 0·001% of lead can be detected and determined in admixture with gold; [44] the method can also be used to discover the location of an impurity in a metal.[45] The arc spectrographic detection and determination of gallium [46] and of germanium [47] are detailed.

Löwe's interferometer, with distilled water as comparison liquid, is well adapted for use in various types of volumetric analysis.[48] The nephelometric determination of lead with chromate has been investigated, with particular reference to its application to toxicological work.[49]

Electrochemical Methods.

Electrolytic.—Minute traces of iodine may be detected by an electrical method, based on depolarisation of the electrode by the iodine, with a consequent increase in current.[50]

A general account has been furnished of the use of the dropping-mercury cathode in electrolytic analysis; [51] it is possible, by using suitable *P.D.*, to determine each of two metals, *e.g.*, bismuth and cadmium, in succession.[52]

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[37] O. Arrhenius and H. Riehm, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, No. 14; **A.**, 1928, 1105.

[38] A. Boutaric and G. Perreau, *Rev. gén. Colloid.*, 1928, **6**, 113; **A.**, 1108.

[39] R. Ehrenberg, *Biochem. Z.*, 1928, **197**, 467; **A.**, 1105.

[40] H. Ley and F. Vanheiden, *Ber.*, 1927, **60**, [*B*], 2341; **A.**, 1928, 51.

[41] K. Jabłczyński and W. Stankiewicz, *Rocz. Chem.*, 1927, **7**, 549; **A.**, 1928, 496. [42] *Idem, ibid.*, p. 534; **A.**, 1928, 496.

[43] H. von Halban and E. Zimpelmann, *Z. Elektrochem.*, 1928, **34**, 387; **A.**, 1109.

[44] W. Gerlach and E. Schweitzer, *Z. anorg. Chem.*, 1928, **173**, 92; **A.**, 859.

[45] *Idem, ibid.*, p. 104; **A.**, 860.

[46] J. Papish and D. A. Holt, *J. Physical Chem.*, 1928, **32**, 142; **A.**, 265.

[47] J. Papish, F. M. Brewer, and D. A. Holt, *J. Amer. Chem. Soc.*, 1927, **49**, 3028; **A.**, 1928, 146.

[48] E. Berl and L. Ranis, *Ber.*, 1928, **61**, [*B*], 92; **A.**, 262.

[49] P. W. Danckwortt and E. Jurgens, *Arch. Pharm.*, 1928, **266**, 374; **A.**, 981.

[50] A. N. Schukarev and Sysoev, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 669; **A.**, 978.

[51] J. Heyrovský, *Bull. Soc. chim.*, 1927, (iv), **41**, 1224; **A.**, 1927, 1159.

Conditions for obtaining an adherent deposit of selenium have been worked out, electrolysis being carried out in presence of known quantities of copper or bismuth.[53] A process for the electrolytic separation of bismuth at low potential is described.[54] Reduction of anodic lead peroxide to monoxide by heat is preferred either to weighing as peroxide or to any process of cathodic deposition.[55] The use of fusible alloy electrodes is described in detail for determining copper, zinc, cadmium, mercury, bismuth, and lead, electrolysis being carried out at a temperature at which the cathode is fluid, the deposited metal forming an alloy with the fusible metal. Deposition is in most cases effected with Wood's metal more smoothly than with a mercury cathode.[56] For the electrolytic determination of zinc in solutions containing sulphuric acid, the preparation of special electrodes is obviated by the addition to the electrolyte of a reducing substance such as alcohol or, better, dextrose.[57] An electrolytic apparatus with special electrodes is described for deposition of minute traces of various metals prior to their characterisation by spectrum analysis.[58]

Potentiometric.—The application of acid ceric sulphate solution as an oxidising agent in potentiometric work has been extensively investigated, and its use for determining vanadium in steel indicated; experiments are recorded with nitrites, iodides, oxalic acid, ferrocyanides, hydrogen peroxide, ferrous iron, arsenic, antimony, tin, titanium, and vanadyl salts.[59] Conversely, cerium salts, after oxidation if necessary, may be titrated with potassium iodide, sodium nitrite, or, preferably, ferrous sulphate.[60] The ceric sulphate solutions are stable and may be kept for long periods if care is taken.

Copper cannot be titrated satisfactorily in aqueous solution with potassium, lithium, sodium, or magnesium ferrocyanide, although results may be improved by working in aqueous alcoholic solutions;[61] in the case of silver, titration with potassium ferrocyanide gives low results, but with the lithium or sodium salts reasonably accurate results are obtained.[62] Indium chloride can be titrated with potassium ferrocyanide, the insoluble compound $KIn_5[Fe(CN)_6]_4$ being presumably formed.[63] With gallium chloride, the precipitate has the composition $Ga_4[Fe(CN)_6]_3$.[64] The same reagent has also been used for lanthanum, cerium, and thorium.[65] Rapid methods have been worked out for the determination of lead and cadmium,[66] and of silver and zinc [67] when present together, ferrocyanide solution being also used in each case. Uranyl acetate, but not the nitrate, can be titrated with ferrocyanide in 30% alcohol and at 70°.[68]

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[52] E. Bayle and L. Amy, *Compt. rend.*, 1928, **186**, 1601; **A.**, 857.

[53] A. Jílek and J. Lukas, *Chem. Listy*, 1927, **21**, 576; **A.**, 1928, 144.

[54] *Idem*, *ibid.*, 541; **A.**, 1928, 146.

[55] A. V. Pamfilov and A. A. Blagonravona, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 699; **A.**, 980.

[56] H. Paweck and R. Weiner, *Z. anal. Chem.*, 1927, **72**, 225; **A.**, 1928, 143.

[57] M. Giordani, *Ann. Chim. Appl.*, 1928, **18**, 63; **A.**, 499.

[58] E. Bayle and L. Amy, *Bull. Soc. chim.*, 1928, (iv), **43**, 604; **A.**, 726.

[59] J. A. Atanasiu, *Bul. Soc. Romane Stiin.*, 1928, **30**, 73; **A.**, 724; J. A. Atanasiu and V. Stefavescu, *Ber.*, 1928, **61**, [*B*], 1343; **A.**, 860; N. H. Furman, *J. Amer. Chem. Soc.*, 1928, **50**, 755, 1675; **A.**, 499, 860; H. H. Willard and P. Young, *ibid.*, 1322, 1334, 1368, 1372, 1376; *Ind. Eng. Chem.*, 1928, **20**, 972; **A.**, 725, 1207.

[60] K. Someya, *Z. anorg. Chem.*, 1927, **168**, 56; *Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 93; **A.**, 146; H. H. Willard and P. Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1379; **A.**, 725; G. Autié, *Bull. Soc. chim.*, 1927, (iv), **41**, 1535; **A.**, 1928, 38.

Potentiometric measurements involving stannous chloride should be carried out in an atmosphere of nitrogen; the reaction with iodine, ferric iron, chromate, ferricyanide, gold, and platinum is given in detail.[69] Chromous sulphate is used for the determination of silver, copper, and gold, alone and together,[70] and similarly for iron, copper, and arsenic in sulphuric acid solution.[71] The iron–dichromate [72] and iron–permanganate [73] reactions have been examined; the principle of the method used in the latter case has also been applied to the silver–halogen reaction.[74] Chromic acid may be determined in the presence of vanadic acid by application of " induction " and catalysis,[75] and methods for hydrogen peroxide and certain associated per-acids are described.[76]

A method for the analysis of hypophosphoric acid depends on the very slight solubility of the uranous salt.[77] Tellurates and tellurites may be titrated potentiometrically with titanous chloride in the presence of hydrochloric acid; in sulphuric acid solution, two breaks are observed with tellurates, the first being the reduction to tellurous acid, but one only in the case of selenates.[78] Details are supplied for the determination of hypochlorous and chlorous acids, especially by potentiometric methods,[79] and for the application of chloramine-T in this class of work.[80] The end-point in the titration of aniline with bromine in neutral solution or with bromate in acid solution is exceedingly sharp,[81] as is usually found for this titration with other substances.

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[61] E. Müller and S. Takegami, *Z. anal. Chem.*, 1928, **73**, 284; **A.**, 499; S. Takegami, *ibid.*, **74**, 39; **A.**, 1928, 860.

[62] W. Speyer, *ibid.*, **74**, 108; **A.**, 859.

[63] U. B. Bray and H. D. Kirschman, *J. Amer. Chem. Soc.*, 1927, **49**, 2739; **A.**, 1928, 38.

[64] H. D. Kirschman and J. B. Ramsey, *ibid.*, 1928, **50**, 1632; **A.**, 861.

[65] J. A. Atanasiu, *Bul. Soc. Romane Stiin.*, 1928, **30**, 51; **A.**, 726.

[66] E. Müller and W. Prée, *Z. anal. Chem.*, 1927, **72**, 195; **A.**, 1928, 38.

[67] E. Müller and H. Hentschel, *ibid.*, p. 188; **A.**, 1928, 37.

[68] J. A. Atanasiu, *Bul. Soc. Romane Stiin.*, 1928, **30**, 77; **A.**, 727.

[69] E. Müller and J. Görne, *Z. anal. Chem.*, 1928, **73**, 385; **A.**, 727.

[70] E. Zintl, G. Reinäcker, and F. Schloffer, *Z. anorg. Chem.*, 1927, **168**, 97; **A.**, 1928, 145.

[71] E. Zintl and F. Schloffer, *Z. angew. Chem.*, 1928, **41**, 956; **A.**, 1109.

[72] F. J. Watson, *Chem. Eng. Min. Rev.*, 1928, **20**, 396; **A.**, 1206.

[73] T. Heczko, *Z. anal. Chem.*, 1928, **73**, 404; **A.**, 726.

[74] *Idem*, *ibid.*, **74**, 289; **A.**, 980.

[75] R. Lang and J. Swerina, *Z. Elektrochem.*, 1928, **34**, 364; **A.**, 982.

[76] A. Rius, *Trans. Amer. Electrochem. Soc.*, 1928, Sept.; **A.**, 977.

[77] W. D. Treadwell and G. Schwarzenbach, *Helv. Chim. Acta*, 1928, **11**, 405; **A.**, 608.

A simple procedure for carrying out certain differential potentiometric titrations is described. The method depends on the change of potential of an indicator electrode; curves and tables are supplied for use in the process, which is capable of great accuracy for the determination of univalent ions.[82] A similar principle has also been utilised by other workers.[83]

The theory of the end-point in acid–alkali titrations has been considered from the mathematical standpoint.[84] A simple and accurate method is given for finding the point of equivalence in those cases when the potential curve has only a slight slope near the end-point or is unsymmetrical.[85]

Various modifications involving metallic electrodes have been made.[86] A study of the applicability and possible errors in the use of the quinhydrone electrode has been made.[87] Details of a sodium amalgam electrode and of the precautions necessary for its use for measuring sodium-ion concentration are given.[88]

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[78] O. Tomiček, *Bull. Soc. chim.*, 1927, (iv), **41**, 1389; **A.**, 1928, 36.

[79] E. Müller and H. Dietmann, *Z. anal. Chem.*, 1928, **73**, 138; **A.**, 497.

[80] A. McMillan and W. Easton, *J. Soc. Chem. Ind.*, 1927, **46**, 472T; **A.**, 1928, 144.

[81] A. V. Pamfilov and V. E. Kisseleva, *Z. anal. Chem.*, 1927, **72**, 100; **A.**, 1927, 1179.

[82] B. Cavanagh, *J.*, 1928, 843, 855; **A.**, 607. Compare *J.*, 1927, 2207; **A.**, 1927, 1045.

[83] D. A. MacInnes, *Z. physikal. Chem.*, 1927, **130**, 217; **A.**, 1928, 36; N. F. Hall, M. A. Jensen, and S. A. Baeckström, *J. Amer. Chem. Soc.*, 1928, **50**, 2217; **A.**, 977.

[84] P. S. Roller, *J. Amer. Chem. Soc.*, 1928, **50**, 1; **A.**, 262; E. D. Eastman, *ibid.*, p. 418; **A.**, 382; F. L. Hahn, M. Frommer, and R. Schulze, *Z. physikal. Chem.*, 1928, **133**, 390; **A.**, 857.

[85] I. M. Kolthoff, *Rec. trav. chim.*, 1928, **47**, 398; **A.**, 496.

[86] E. Müller and H. Kogert, *Z. physikal. Chem.*, 1928, **136**, 437, 446; **A.**, 1203; N. H. Furman, *J. Amer. Chem. Soc.*, 1928, **50**, 268, 273; **A.**, 383; N. H. Furman and E. B. Wilson, jun., *ibid.*, p. 277; **A.**, 382; J. O. Closs and L Kahlenberg, *Trans. Amer. Electrochem. Soc.*, 1928, Sept.; **A.**, 1203.

[87] A. Rabinovitsch and V. Kargin, *Papers Pure Appl. Chem. Karpov Inst., Bach Festschr.*, 1927, 3; **A.**, 1928, 382; *Z. Elektrochem.*, 1928, **34**, 311; **A.**, 1106; A. Klit, *Z. physikal. Chem.*, 1927, **131**, 61; **A.**, 1928, 143.

[88] G. Ettisch and K. Joachimsohn, *Z. Elektrochem.*, 1928, **34**, 404; **A.**, 1108.

BIOCHEMISTRY.

THE policy adopted in recent years of reporting on a limited number of divisions in plant and agricultural chemistry and in animal chemistry has been continued. Since, during the last two or three years, subjects of more immediate practical importance have been reviewed in the section devoted to the chemistry of the plant, it seemed opportune to review this year matters that are at present of more academic interest. In accordance with this policy there will be found in this Report a somewhat extensive review of recent progress in certain fields of protein chemistry. The data upon which this part of the Report is based are not exclusively derived from plant chemistry, although it has been prepared by the Reporter responsible for the plant side. On the other hand, in the case of certain subjects (*e.g.*, phosphoric esters formed in yeast fermentations), included for convenience of discussion in the animal section, the data drawn upon have been in part derived from what might legitimately be regarded as plant chemistry. The space devoted to protein chemistry in the one section and to the chemical processes occurring in muscle in the other section necessarily curtails the space available for the discussion of less well co-ordinated fields of research. Such curtailment is inevitable at times if certain aspects of general biochemistry are to be adequately presented and the Reporters feel that no apology is needed. Nor do they feel that any apology is required for the fusion under the ægis of one Reporter of fields of cognate interest irrespective of their strict plant or animal origin.

Enzyme Activity of Resting Bacteria.

An account was given in the Report for 1926 [1] of Quastel's theory that hydrogenations effected by bacteria are primarily due to polarisations of substrate molecules induced by electric fields which characterise particular centres—the "active centres"—of cellular and intracellular surfaces. Quastel and Wooldridge have further investigated and developed this theory, and the main results of this important study have been recently summarised by the former.[2]

Whether a particular molecule is activated or not at a centre depends upon the nature and strength of the polarising field at the centre and upon the nature of the substrate molecule. When activation of a substrate molecule (hydrogen donator) occurs, the following equations represent the events which follow: (1) $D \rightleftharpoons A_a'' + 2H^{\bullet}$, (2) $A_a \rightleftharpoons A$, where D is the hydrogen donator, A is the oxidised form after loss of 2H, and A_a is the activated form of the molecule which can only exist as such in the presence of the polarising field. The act of oxidation consists in the transference of electrons from A_a'', the electrically neutral molecule A_a being transposed into the normal form A out of contact with the field. The system thus becomes amenable to the same theoretical treatment as any system which gives rise to a reduction or oxidation potential.[3] The development of this hypothesis leads Quastel and Wooldridge to consider the specificity and mechanism of enzyme action. Specificity of action they think depends on three factors: (1) Specificity of adsorption at the activating centre, (2) the nature and strength of the polarising field at the centre, (3) the constitution of the adsorbed molecule.[4] These conclusions are substantiated by much experimental work with *B. coli*, which shows that these active centres or enzymes in the cell surface are not all inactivated under the same conditions, and that they possess specific differences in their power of adsorbing compounds characterised by the possession of a particular structure. Thus the centres (enzymes) which activate lactic acid as a hydrogen donator adsorb compounds characterised by $\cdot CO \cdot C \cdot OH^*$ or $\cdot CH(OH) \cdot C \cdot OH^*$, where H^* is mobile and the substance acidic, whilst the centres for succinic acid adsorb compounds with $\cdot C \cdot CH \cdot CO \cdot OH$ or $C \cdot CH_2 \cdot CO \cdot OH$ structures. They consider that the centres of activity of the cell are simply a property of the surface structures of the colloidal materials which make up the cell as a whole, and that the actual magnitude of this structure is of no great significance. It may be small enough to be classed as "soluble" and to pass through a membrane, or large enough to be classed as "insoluble." The distinction is one of degree, and the smaller structure has less chance of possessing a number of different centres than a large one (resting bacteria). That enzyme action is due to active centres receives support from the observation that preparations from *B. coli* of "soluble" lactic acid enzymes have the same specific adsorbing power on a particular type of compound as has the lactic acid centre (enzyme) of similar (resting) bacteria.[5] It is of interest to compare their hypothesis with a statement of Willstätter,[6] taken from a lecture delivered before the Chemical Society last year:

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[1] *Ann. Reports*, 1926, **23**, 245.

[2] *J. Hygiene*, 1928, **28**, 139.

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[3] *Biochem. J.*, 1927, **21**, 148; **A.**, 1927, 280.

[4] *Ibid.*, p. 1224; **A.**, 1927, 1113.

[5] *Ibid.*, 1928, **22**, 689; **A.**, 797; Stephenson, *ibid.*, p. 605; **A.**, 549.

[6] *J.*, 1927, 1374.

" It seems that we must consider an enzyme to be composed of a specifically active group and a colloidal carrier. . . . The colloidal carrier seems to vary somewhat in its nature, but to be necessary for the stability of the active group." Willstätter's conclusions are based on the separation and purification of " soluble " enzymes, and differ from those of Quastel and Wooldridge only in emphasising an active group instead of an active centre. Cook and Woolf [7] have further investigated the observation of Quastel and Woolf [8] that *B. coli* under anaerobic conditions can effect a reductive deamination of aspartic acid to succinic acid, and that under the influence of growth inhibitors such as toluene the following reversible equilibrium is established : aspartic acid $\rightleftharpoons$ fumaric acid + ammonia. Eleven other bacteria have been shown to bring about the former reduction, but the equilibrium is only established by the four facultative anaerobes and appears to be specific for aspartic acid. It is suggested that two distinct mechanisms capable of dealing with this amino-acid are present in bacteria. The observation is of great interest not only because biological synthesis of amino-acids has hitherto been effected only by perfusion of the isolated liver with α-ketonic or hydroxy-acids, but because it may help to explain the connexion in plant metabolism between the succinic acid produced by oxidation of fats and sugars and the accumulation of asparagine which occurs when excess of nitrogen is present.

Aerobic and Anaerobic Oxydases.

Pugh and Raper [9] have recently suggested a convenient, but admittedly provisional classification of the oxydases. Those which act only in the presence of oxygen or a peroxide, and comprise peroxydase, tyrosinase, and the thermostable catalysts known as polyphenolase, are referred to as aerobic oxydases, whereas the oxido-reductases (dehydrases) and the thermostable catalysts working in conjunction with glutathione, which will act anaerobically provided a suitable hydrogen acceptor is present, are referred to as anaerobic oxydases.

Raper has recently reviewed the present knowledge of the aerobic oxydases.[10] Bach and Chodat's well-known theory of the dual nature of the direct plant oxydases—in which the oxygenase is regarded as an oxygen carrier which forms a peroxide on exposure to air, which can then be activated by peroxydase—and Onslow's modification—which suggests that oxygenase is really a mixture of an enzyme and a pyrocatechol derivative which react together in the presence of air to give a peroxide—are subjected to considerable criticism. Raper points out that the guaiacum reaction is given by five oxidation systems the components of which may and do occur together in many plant-tissues, and suggests that the oxygenase of Onslow is either tyrosinase or a polyphenase of the laccase type. Both of these oxidise pyrocatechol in the air to produce *o*-benzoquinone and if guaiacum is added it will be turned blue. This view is contested by Onslow and Robinson,[11] who maintain their claim that higher plants contain an enzyme giving the "direct oxydase reaction" with guaiacum which catalyses the auto-oxidation of *o*-dihydroxy-compounds with the probable production of hydrogen peroxide and *o*-benzoquinone, and see no reason for discarding the term "oxygenase" for the enzyme which primarily catalyses the *o*-dihydroxy-group. The investigations of Raper [12] into the production of melanin from tyrosine by tyrosinase have now been brought to a successful conclusion. Some of the tentative suggestions put forward in 1926 [9] have not been substantiated and Raper now puts forward the following series of reactions :

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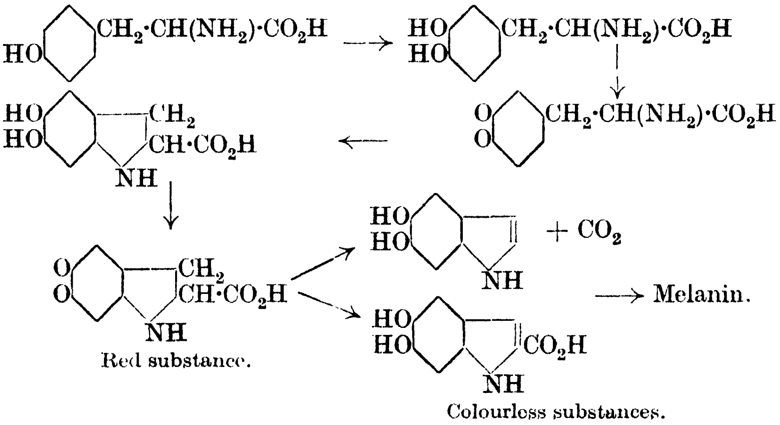
[7] *Biochem. J.*, 1928, **22**, 474; **A.**, 551.

[8] *Ibid.*, 1926, **20**, 545; **A.**, 1926, 868.

[9] *Ibid.*, 1927, **21**, 1370; **A.**, 1928, 202.

[10] *Physiol. Reviews*, 1928, **8**, 245.



3 : 4-Dihydroxyphenylalanine, the first product of the reaction, is oxidised to the corresponding quinone. By intramolecular arrangement, followed by oxidation, the 5 : 6-quinone of 2 : 3-dihydroindole-2-carboxylic acid is formed, which is believed to be the red substance, the first visible product of the reaction. The enzyme is necessary for the production of this substance, but it is not required for the further oxidation to melanin. If the decoloration of the red compound is rapid, 5 : 6-dihydroxyindole-2-carboxylic acid is formed; if it is slow, as happens in an inert

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[11] *Biochem. J.*, 1928, **22**, 1331; **A.**, 1282.

[12] *Ibid.*, 1927, **21**, 89; **A.**, 1927, 278.

atmosphere at room temperature, then carbon dioxide is lost and 5 : 6-dihydroxyindole is produced. The actual constitution of melanin is still obscure, and it is not yet certain if the melanins found in animal cells are produced by a similar series of reactions, but the existence in the melanoblasts of the epidermis of the skin of an enzyme (apparently not tyrosinase) which produces a melanin from 3 : 4-dihydroxyphenylalanine, and the presence of that amino-acid in the wing coverings of cockchafers, is strong evidence in support of this theory. The function of tyrosinase in the plant still remains obscure : the suggestion of Szent-Györgyi [13] that it is of importance in the respiratory processes of plants has been shown by Platt and Wormall [14] to be untenable.

Recent research in the field of anaerobic oxydases has centred round the specificity of the various dehydrases. The succino-dehydrase was first extracted from muscle by Ohlsson [14a] and was found to convert succinic acid in the presence of methylene-blue partly into fumaric and partly into malic acid. It has now been shown that this is due to the presence of two separable enzymes,[15] succino-dehydrase, which converts the succinic acid into fumaric acid, and fumarase, which will bring about a reversible equilibrium between fumaric and malic acids.

Hahn and Haarman [16] have shown that washed minced muscle in the presence of methylene-blue will dehydrogenate malic acid to oxalacetic acid, which was isolated as the semicarbazone. This observation is of interest in view of the fact that Quastel was unable to demonstrate it with resting *B. coli*, although measurements of the gaseous exchange suggested that it must be an intermediary product in the fermentation by that organism of succinic acid to acetic acid.[17]

Lactic dehydrase has been prepared from *B. coli* by Stephenson [18] and from yeast by Bernheim.[19] Both these preparations act slowly on α-hydroxybutyric acid, but the reaction products have not been identified. Hahn, Fischbach, and Haarman [20] show that washed minced muscle will effect the dehydrogenation of lactic to pyruvic acid, which was isolated as the phenylhydrazone. Bernheim [19] also claims to have isolated a citric acid dehydrase from liver.

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[13] *Biochem. Z.*, 1925 **162**, 399; **A.**, 1926, 99.

[14] *Biochem. J.*, 1927, **21**, 26; **A.**, 1927, 384.

[14a] *Skand. Arch. Physiol.*, 1921, **41**, 77.

[15] Alwall, *ibid.*, 1928, **54**, 11; *Physiol. Abs.*, 1928, 349; Clutterbuck, *Biochem. J.*, 1928, **22**, 1193; **A.**, 1281.

[16] *Z. Biol.*, 1928, **88**, 91; **A.**, 1281.

[17] *Ann. Reports*, 1925, **22**, 231.

[18] *Biochem. J.*, 1928, **22**, 605; **A.**, 549.

[19] *Ibid.*, p. 1178; **A.**, 1281.

[20] *Z. Biol.*, 1928, **88**, 89; **A.**, 1281.

It was stated by Michlin[20a] that the aldehyde oxydase which he prepared from potato by precipitating the watery extract with acetone would reduce nitrate, but not methylene-blue. Bernheim[21] has now shown that, if regard be paid to the p_H, reduction of the dye does take place. The enzyme can therefore be classified as a dehydrase, as can also the xanthine oxydase. Bernheim has recently discussed the specificity of the dehydrases, and inclines to the view that each substrate has its specific enzyme, *i.e.*, according to Quastel's theory it is activated by adsorption at specific active centres. He admits, however, that the evidence is not conclusive, for it would then be necessary to assume that xanthine oxydase consists of two entities, an aldehyde oxydase and a purine oxydase. No evidence of this has been detected by Dixon and Kodama,[22] who have concentrated the milk enzyme 4000 times.

With regard to the function of the anaerobic oxydases it is generally accepted that they activate hydrogen in the substrate on which they act, that is, they may convert substances such as succinic acid, which are not usually regarded as reducing agents, into such. Further, there is evidence that they activate molecular oxygen. Raper[23] considers that under these conditions of widened oxidation–reduction potential the succinic acid, or in living cells even more stable substances such as saturated fatty acids, can be oxidised. As Thunberg[24] finds evidence of these enzymes in the higher plants, their presence in the protoplasm of living cells is probably universal, and it becomes of interest to inquire whether reduction potentials have been observed in living cells.

Hydrogen-ion Concentration and Reduction Potentials of Living Protoplasm.

It is essential that the normal condition of the protoplasm be maintained when either of these factors is being determined. The first to realise this condition experimentally were Needham and Needham,[25] who made use of the new micrurgical technique developed by Chambers. By micro-injection of appropriate dyes they were able to show that the internal p_H of a number of species of marine ova was 6·6 and that this value fell to below 5·0 on cytolysis of the cell. They showed later[26] that the p_H of *Amœba proteus* was about 7·6, and that the cell was not only capable of reducing the oxidised forms of indicators of more positive potential but also of oxidising the leuco-forms of indicators of oxidation-reduction potential lower than its own, and that there was a fairly constant reduction potential zone lying between r_H 17 and 19, which they concluded was widely independent of the concentration of oxygen in the external atmosphere. Chambers, Pollack, and Hillar[27] found that the internal p_H of both *A. proteus* and *A. dubia* was 6·9 ± 0·1, that they possessed considerable buffering capacity, and that a significant change of p_H was associated with the death of the cell. Extending their studies with starfish eggs, Chambers and Pollack[28] differentiate between the p_H of the cytoplasm, which was 6·7 ± 0·1, and of the nucleus, which was 7·5 ± 0·1. More recently Cohen, Chambers, and Reznikoff[29] have determined the reduction potentials of *A. dubia* and their results are only in partial agreement with those of the Needhams. They consider that in interpreting reduction phenomena of micro-injection it is necessary to take into consideration the intensity, capacity, and rate factors. We shall deal with these points in turn. 1. *Reduction intensity.* Under anaerobiosis the amœba develops in its interior a high, primary reducing potential with a value certainly less than r_H 7·6. Under aerobiosis the neutralising effect of the atmospheric oxygen shifts the r_H to any value between 13 and 18, depending on secondary factors. This range corresponds to the well-known effect found in aerated suspensions of cells, namely, a gross reducing intensity stabilised between 0·1 and 0·2 volt at p_H 7·0.[30] 2. *Reducing capacity.* Under anaerobiosis the amœba appears to contain only active reductants, and therefore has no poising ability. Interference of oxygen complicates the picture by introducing oxidants of all shades of activity and elaborated presumably at varying rates. 3. *The rate factor.* The danger of applying to the dynamic activity of the heterogeneous system of the cell some of the criteria established for essentially static, homogeneous indicator systems is recognised, as these require the introduction of a time factor. Despite the complexity of the subject, the authors consider that the almost instantaneous reduction of the indicators on the electropositive side is strong evidence for the existence of a virtual labile, reversible equilibrium state.

[20a] *Biochem. Z.*, 1927, **185**, 216; **A.**, 1927, 699.

[21] *Biochem. J.*, 1928, **22**, 344; **A.**, 550.

[22] *Ibid.*, 1926, **20**, 1104; **A.**, 1926, 1175.

[23] *Physiol. Reviews*, 1928, **8**, 245.

[24] XII*th Int. Cong. Physiol.*, 1926, 161; **A.**, 1928, 550.

[25] *Proc. Roy Soc.*, 1926, *B*, **99**, 173; **A.**, 1926, 194.

[26] *Ibid.*, p. 383; **A.**, 1926, 545.

All these micrurgical studies suggest that there is a uniform p_H and r_H distributed throughout the cytoplasm of these simple cells. In accepting this conclusion the limits of the methods employed, resting as they do on colour changes observed under the microscope, must be kept in mind (Cohen, Chambers, and Reznikoff discuss them in great detail). In living cells the protoplasmic proteins are within, or not far away from, their isoelectric range; consequently a small local change of p_H may have a pronounced effect on their physical properties. Protoplasmic streaming is itself almost sufficient proof that such local changes must occur, and there is also the observation of Osterhout,[31] referred to in last year's Report, showing a difference of potential of 14·5 millivolts across the protoplasm of *valonia*. That the dye injection method is still too crude to permit one to follow possible local changes of metabolic activity is also apparent. Fertilisation of the egg of the sea urchin is known to be followed by an enormous increase in the oxygen consumption, yet the Needhams failed to observe any coincident decrease in the r_H. Cannan [32] has pointed out that a change of two or three units of r_H, which the method is incapable of observing, corresponds to an increase of several hundredfold in the concentration of the reduced pigment (echinochrome), and therefore of oxygen consumption. The possible presence of large local gradients of r_H also follows from another observation of Cannan's [33] connected with the oxidation–reduction indicator hermidin, which is present in the leaf cells of *Mercurialis*. The indicator is held 95% reduced, corresponding to r_H 10 and an oxygen pressure of only 10^{-60} atmosphere. Yet during photosynthesis the chloroplasts must be in equilibrium with atmospheric oxygen. Now oxygen does not appear to exert anything like its full potential in biological systems, and Cannan, Cohen, and Clark [30] assign to "biological oxygen" an oxidation intensity of about r_H 18. This would still give a difference of potential of at least 0·2 volt between the chloroplasts and the vacuole sap containing the hermidin. Bearing these facts in mind, it would appear that the conditions of p_H and r_H in the cell may be far from uniform and that the expression "isoelectric point" of the cell, used by certain physiologists, has very little, if any, significance.

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[27] *Proc. Soc. Exp. Biol. Med.*, 1926–7, **24**, 760.

[28] *J. Gen. Physiol.*, 1926–7, **10**, 739; **A.**, 1927, 696.

[29] *Ibid.*, 1928, **11**, 585; **A.**, 793.

[30] *U.S. Pub. Health Ser.*, 1926, Suppl. 55, 1; **A.**, 1926, 1009.

The Transport of Organic Substances in Plants.

One of the chief reasons why our present knowledge of plant metabolism is inferior to that of animal metabolism is the lack of first-hand information as to the channels of transport of material in the plant, and of the chemical nature of the substances transported. The sap flowing from one part of a plant to another, which would yield information corresponding to that given by the blood and lymph of animals, cannot be obtained in any quantity from a plant without injury; consequently to gain some knowledge of the general problem of translocation in the plant the physiologist has had to rely on external observation and histological research, and the chemist has had to be content with gross analyses of tissues. Until recently the subject remained one of purely academic interest, but there is now increasing evidence that many agricultural problems demand as an aid to their solution a greater knowledge of this question than we at present possess. As examples of work published during the present year may be mentioned that of Rosa,[34] who finds that tomato plants suffering from Western yellow blight accumulate excess of carbohydrate in a manner which suggests that they have lost the power of translocating nitrogen, and of Johnston and Dore,[35] who show that in the same plants boron deficiency leads to a breakdown of the conducting tissues and an accumulation of sugars in the leaves. Its importance has been recognised by Mason and Maskell,[36] working at the Cotton Research Station, Trinidad, who have published during the year two papers of outstanding interest dealing with the transport of carbohydrates in the cotton plant.

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[31] *Ann. Reports*, 1927, **24**, 236.
[32] *Biochem. J.*, 1927, **21**, 184; **A.**, 1927, 271.
[33] *Ibid.*, 1926, **20**, 927; **A.**, 1926, 1183.

For many years now the view has been widely held that (briefly stated) the sugars and other products manufactured in the leaf are distributed about the plant by means of the sieve tubes, and that the tracheæ of the wood serve only for the upward transportation of materials from the root system. Dixon [37] recently reviewed the whole question, and showed that, if the organic matter necessary for the growth of a potato tuber was translocated downwards solely through the sieve tubes, a 10% solution of sugar would have to move at about 50 cm. per hour. Such a rate seems incredible, and Dixon suggested that the wood alone admits of such high rates of mass movements of solution. To test, if possible, the validity of this assumption Mason and Maskell,[36] in a well-planned series of experiments, have attempted to follow the movement of carbohydrates in the cotton plant by regional analysis of the tissue. The results of many hundreds of analyses of " total carbohydrates," " total reducing sugars," and sucrose are statistically presented. Examination of the diurnal variations shows that the variation in the total concentration of sugars in the leaf can be correlated more readily with that in the bark (which contains the sieve tubes) than the wood. By ringing the stem and also by partial stripping of the bark they show conclusively that the downward movement of sugar from the leaves takes place in the bark along a well-marked gradient in sugar concentration, and that the direction of this movement can under certain conditions be reversed. Further, examination of the radial distribution of sugars in the bark shows that there is a high positive correlation between the percentage of sieve tubes in any one zone of bark and the sucrose concentration in that zone. Their results leave but little doubt that the transport of sugar takes place in the sieve tubes, and that most of the sugar is transported as sucrose. Further, they show, by calculations based on rates of transport of sugars and gradients of sugar concentration, that the sugar moves in the sieve tubes by a process analogous to diffusion, but the observed diffusion constant of sugar in the sieve tubes is about 40,000 times as great as the diffusion constant for sugar in a 2% solution of sucrose in water. If sugar in the sieve tubes can move at such high rates, then Dixon's 50 cm. per hour may not be so improbable; even so, to quote Mason and Maskell, " . . . the problem of the exact mechanism by which such high absolute rates of movement are maintained remains quite unsolved."

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[34] *Plant Physiol.*, 1927, **2**, 163; *Physiol. Abs.*, 1928, **66**.

[35] *Science*, 1928, **67**, 324. [36] *Ann. Bot.*, 1928, **42**, 189, 571; **A.**, 559, 1061.

[37] *Brit. Assoc. Reports*, 1922, 193.

Chemical Composition of Apples.

In last year's Report attention was directed to the great commercial importance of the investigations which are being undertaken in this country to determine the factors which favour or prevent deterioration of fruit in storage. The Report of the Food Investigation Board for the year 1927 [38] deals very fully with apples, and much of the research described is of biochemical interest.

The well-established fact that the good keeping quality of apples is associated with slow consumption of respirable material suggests that the onset of physiological disease during storage is due to exhaustion of some substances necessary to the process of respiration, either as food or as catalyst. Investigations of losses of dry weight of apples kept in store are shown by Haynes and her co-workers [39] to be losses of sugar and acid only. They show further that the percentage of acid lost was low when nitrogen was low, and that the percentage of sucrose inverted per unit of nitrogen was directly related to the acid originally present. Internal breakdown in cold storage they consider depends on whether the amount of sucrose falls below that required by the apple. Cold storage retards the inversion of sucrose in a marked way. In apples with a low nitrogen (protoplasmic) content the rate of inversion is more rapid than that of oxidation, and the keeping quality is good. High nitrogen, on the other hand, involves a large consumption of sugar, and the amount of sucrose inverted in a given time may be so reduced at 1° that it is insufficient to meet the demands made on it. Internal breakdown then occurs, and death of the apple results. Gas storage at 8° has a retarding effect on the consumption of sucrose in apples, and probably owes its value largely to this fact. Some interesting research into the chemical composition of apples has been carried out recently in America by Caldwell,[40] who has attempted to find out what effect climate and temperature have on the chemical composition of apple juice. The quality of dessert fruit is considered to depend on the total sugar, sucrose, and acid content of the juice, and is highest when these are highest. The theory, which is widely held in America, that every variety of apple has an optimum mean summer temperature, at which it attains its best development, is confuted. The composition of the fruit of all varieties shows considerable variation from year to year; the direction and extent of these variations are determined by opportunities for photosynthesis, and the response to this is similar in all varieties, whether grown at high or low temperatures. Seasonal amount of sunlight, then, is the determining factor, and not temperature. As there is an increasing appreciation in America of unfermented apple juice as a beverage, the question of blending juices to attain the requisite palatability has naturally had to be considered. This quality seems to depend on the relative amounts of total sugar, free acid, and astringent substances present. Varieties of apples which will give the necessary balance of total sugar and acid can easily be obtained in America. Caldwell shows that sunshine is again the most potent factor, and that a high annual average for sunshine and temperature produces increased sugar and acid contents, and decreases astringency. For blending purposes it is necessary to have some varieties of apples possessing a high astringent value. As the usual American apple varieties are useless for this purpose, Caldwell has studied the effect of foreign varieties. French cider apples are shown to be the most suitable, as they retain their high free-acid and astringent values even after 23 years' growth on American soil. Those who prefer their fruit juices fermented will no doubt find J. T. Hewitt's [41] monograph on "The Chemistry of Wine Making" more to their taste.

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[38] D.S.I.R., H.M. Stat. Office, 1928.

[39] *Ann. Bot.*, 1928, **42**, 1, 29, 541; **A.**, 558, 558, 802; *Biochem. J.*, 1928, **22**, 947; **A.**, 1061.

The Structure of the Protein Molecule.

Amino-acids.—During the year under review two new amino-acids have been added to the list of the well-established amino-acids derived from proteins. Harington[42] has resolved thyroxine (see also p. 261) and is satisfied that it is a primary constituent of thyroglobulin. In 1922 Mueller[43] described the isolation from several proteins of a sulphur-containing amino-acid which appeared to have the empirical formula $C_5H_{11}O_2NS$. Barger and Coyne[43a] have recently synthesised the substance $CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ and have shown that it is identical with Mueller's amino-acid. Mueller has agreed with Barger's suggestion that the new amino-acid should be called methionine.

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[40] *J. Agric. Res.*, 1928, **36**, 289, 367, 391, 407; **A.**, 802, 802, 1061, 1061.

[41] Empire Marketing Board, No. 7, H.M. Stat. Office, 1928.

In addition, several important papers dealing with the purification and properties of already well-established protein amino-acids have appeared. Proline has always been one of the most troublesome amino-acids to estimate in the products of hydrolysis of proteins. Separation by means of absolute alcohol is laborious, and crystallisation of the resulting product difficult. Values for total proline content of proteins (based on isolation of copper proline or proline hydantoin) have always been considered too low, so that new methods for the rapid isolation of crystalline proline are very welcome. Town[44] first prepares the copper salts of the amino-acids of the protein digest, dehydrates these with acetone, and separates that of proline by taking advantage of its solubility in cold methyl alcohol. Pure *l*-proline is obtained as a white non-deliquescent solid melting with decomposition at 215° and having $[\alpha]_D^{18^\circ} = -86{\cdot}8^\circ$, higher than the value previously recorded. Kapfhammer and Eck[45] also have given a method of preparation based on Reinecke's salt.[46] Lysine, which has hitherto not been obtained in the free state, is usually isolated as the picrate. Vickery and Leavenworth[47] have now shown that if the base is adequately purified (through the picrate) and is protected from carbon dioxide it crystallises readily in needles which decompose at 224° and have $[\alpha]_D^{20^\circ} = +14{\cdot}6^\circ$. They have also improved the technique for the crystallisation of free arginine and free histidine.[48] Other valuable papers dealing with the preparation in bulk of the individual hexone bases should be noted.[49] The four dissociation constants of cystine have been determined by Cannan and Knight.[50]

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[42] Private communication.

[43] *Ann. Reports*, 1922, **19**, 184.

[43a] In the press; referred to by Vickery and Osborne, *Physiol. Rev.*, 1928, **8**, 393.

[44] *Biochem. J.*, 1928, **22**, 1083; **A.**, 1148.

[45] *Z. physiol. Chem.*, 1927, **170**, 294; **A.**, 526.

[46] *Ibid.*, p. 289; **A.**, 542.

[47] *J. Biol. Chem.*, 1928, **76**, 437; **A.**, 400.

[48] *Ibid.*, p. 701; **A.**, 511.

[49] Vickery and Leavenworth, *ibid.*, 1928, **78**, 627; **A.**, 1121; Kapfhammer and Spörer, *Z. physiol. Chem.*, 1928, **173**, 245; **A.**, 657; Cox, *J. Biol. Chem.*, 1928, **78**, 475; **A.**, 993.

[50] *Biochem. J.*, 1927, **21**, 1384; **A.**, 1928, 128.

From a consideration of the solubility of isoelectric cystine, Andrews and E. J. de Beer [51] postulate the existence of four isomerides.

A new method for determining phenylalanine by oxidation to benzoic acid with potassium dichromate in acid solution has been described.[52]

Separation of the Hexone Bases.—The classical method devised by Kossel and Kutscher [53] and modified by Kossel and Patten [54] was based on the assumption that only the hexone bases were precipitated by phosphotungstic acid in acid solution, and that the silver salts of arginine and histidine were precipitated at different degrees of alkalinity. Three fractions were obtained, from which lysine was isolated and weighed as picrate, and the other two bases estimated by determination of nitrogen in their respective fractions. The accurate determination of these three bases is of the greatest importance in view of recent developments in the physical chemistry of proteins, so a reinvestigation of the problem by Vickery and Leavenworth [55] is particularly welcome. Their investigation has been very thorough, and a complete account of their results and their criticisms of the older methods cannot be given here. Briefly, they show: (1) Phosphotungstic acid in acid solution does not precipitate the whole of the arginine and lysine. (2) Both these bases (under certain conditions) can be quantitatively precipitated from the hydrolysate as silver salts. Precipitation with phosphotungstic acid is unnecessary except in the case of lysine, which is known to give a much less soluble phosphotungstate. (3) The silver salts of arginine and histidine can be sharply separated at p_H 7·0, the histidine being completely precipitated. Each base is then converted into the crystalline dinitronaphtholsulphonate and weighed. (4) An accurate determination of the bases cannot be made with a sample of protein less than about 350 grams. With the customary sample of 50 grams the results are about 10% low. (5) Their results compared with those obtained by the Van Slyke method show agreement only in the case of arginine: the other bases are lower. The following table gives the results of their analysis of edestin together with that of Kossel and Patten.

	Per cent. of protein.		
	Arginine.	Lysine.	Histidine.
Vickery and Leavenworth	15·68	1·97	2·16
Kossel and Patten	14·17	1·65	2·19

Such differences may at first sight seem small, but in relation to the chemistry of the protein molecule they are of prime importance, as is exemplified by the analysis of the bases of horse hæmoglobin.[56] The iron content of this protein leads to a minimal molecular weight of 16,670, and the sulphur content to 8,220. The recent ultracentrifuge experiments of Svedberg and Fahraeus [57] and osmotic experiments of Adair [58] leave little doubt that the true value is around 66,800. Accepting the latter figure, the agreement between the calculated and the found values for the number of molecules of the respective bases is as follows :

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[51] *J. Physical Chem.*, 1928, **32**, 1031; **A.**, 950.

[52] *Biochem. Z.*, 1928, **194**, 1.

[53] *Z. physiol. Chem.*, 1900, **31**, 165.

[54] *Ibid.*, 1903, **38**, 39.

[55] *J. Biol. Chem.*, 1928, **76**, 707; **A.**, 511.

	Number of molecules.	Calculated.	Found.
Histidine	33	7·66	7·64
Arginine	12	3·13	3·11
Lysine	37	8·09	8·10

Such data show, first, that, as these molecular proportions are not divisible by four, the hæmoglobin molecule is not formed of four symmetrical parts. Secondly, they enable biologists to calculate with a fair degree of certainty the acid-binding capacity of the blood proteins. Equally exact methods are now urgently required for the determination of the dicarboxylic acids—especially of hydroxyglutamic acid. A micro-method for determining Hausmann numbers that may be of use in characterising small amounts (0·1 gram) of proteins has been devised by Thimann.[59]

Estimation of Amino-nitrogen.—Foreman [60] has published a very ingenious method of estimating certain " groups " in biological fluids, which is an elaboration of his earlier method of titrating amino-acids in the presence of a large excess of alcohol.[61] Whilst offering no advantages in the estimation of the amino-nitrogen in protein hydrolysates, the method should find wide application in plant and bacterial chemistry, since for the first time it enables us to determine volatile bases (including ammonia), non-volatile amines, and amino-acids, besides certain other " acidities " which are useful for purposes of comparison.

Linderström-Lang [62] has recently discussed from a practical standpoint the theory of the titration of amino-acids and, having selected on theoretical grounds the requisite indicator, naphthyl-red, has shown that all the free amino-groups of the naturally occurring protein amino-acids can be quantitatively titrated in 90% acetone with $N/10$-alcoholic (90%) hydrogen chloride. Sörensen [63] has used the method in his recent enzyme studies

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[56] *J. Biol. Chem.*, 1928, **79**, 377.

[57] *J. Amer. Chem. Soc.*, 1926, **48**, 430; **A.**, 1926, 340.

[58] *Ibid.*, 1927, **49**, 2524; **A.**, 1927, 1212.

[59] *Biochem. J.*, 1926, **20**, 1190; **A.**, 1927, 66.

[60] *Ibid.*, 1928, **22**, 208; **A.**, 448. [61] *Ibid.*, 1920, **14**, 451.

[62] *Compt. rend. Trav. Lab. Carlsberg*, 1928, **17**, 1; **A.**, 313.

[63] *Ibid.*, No. 7; **A.**, 922.

(see p. 245) and states that in the presence of proteins or their more complex derivatives it is superior to the method of Van Slyke.

It may be advisable here to call attention to the developments that have recently taken place in respect to the theory of the dissociation of ampholytes, as these have an important bearing on the significance to be attached to the dissociation constants of amino-acids. The older conception postulated that the constant involved in the titration of an amino-acid in the acid range of p_H concerned the amino-group, and was therefore referred to as the basic dissociation constant, pk_b. Similarly titration in the alkaline range gave the acid dissociation constant pk_a. In the isoelectric range the ampholyte was considered to be practically undissociated. Adams[64] was the first to suggest that the reverse significance should be attached to these constants. Bjerrum[65] has more recently advocated the same views and regards the amino-acid in neutral solution (" undissociated ") as present almost entirely as " Zwitterion " $^{+}NH_3{\cdot}R{\cdot}CO{\cdot}O^{-}$. On the addition of acid the ionisation of the $R{\cdot}CO{\cdot}O^{-}$ groups is suppressed and $^{+}NH_3{\cdot}R{\cdot}CO{\cdot}OH$ ions are formed. Consequently a titration through the acid range of p_H involves the acid group, and not the basic group, as was hitherto supposed. Similarly, the titration through the basic range of p_H leads to the formation of $NH_2{\cdot}R{\cdot}CO{\cdot}O^{-}$ ions, and involves the basic group. The dissociation constants determined by titration from strongly acid to strongly basic range of p_H are designated usually as pK'_1, pK'_2, etc., without defining the nature of the groups involved, and in the case of a monoamino-monocarboxylic acid such as glycine pK'_1 becomes the dissociation constant attached to the carboxyl group and pK'_2 to the amino-group. The new constants are related to the older ones in the following way : $pK'_1 = pk_w - pk_b$ and $pK'_2 = pk_a$. Bjerrum's views lead to a much more rational explanation of the behaviour of amino-acids and proteins in solution than those hitherto employed, and their general adoption by those engaged in protein research and by authors of text-books on biochemistry is to be recommended.

Brönsted's treatment of ampholytes, based on the following relation between acid (S), base (B), and hydrogen ion (H^+), $B + H^+ \rightleftharpoons S$,[66] has been used with advantage by Linderström-Lang,[62] whose paper contains a discussion (in English) of its application to the titration of amino-acids.

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[64] *J. Amer. Chem. Soc.*, 1916, **38**, 1503.

[65] *Z. physikal. Chem.*, 1923, **104**, 147; *A.*, 1923, i, 444.

[66] *Rec. trav. chim.*, 1923, **42**, 718.

Recent Researches into the Structure of the Protein Molecule.

During the past few years a bewildering number of papers have appeared which seek to throw fresh light on the constitution and structure of the protein molecule. Abderhalden has been particularly active in this field, and one is grateful for the review by Klarmann,[67] which is more or less an exposition of Abderhalden's views. Briefly stated, his hypothesis is that proteins are essentially complex compounds of which the components are substances containing amino-acids which are, in part at least, in peptide-anhydride union with each other. It is supported by experiments upon partly hydrolysed proteins which show: (1) diketopiperazines can be isolated from such material; (2) piperazines can be isolated if the material is previously reduced with sodium and alcohol; (3) positive colour reactions for diketopiperazines can be obtained; (4) oxamide can be obtained after oxidation of the material with permanganate. Vickery and Osborne [68] have also recently published a review of hypotheses of the structure of the protein molecule, in which the views of Abderhalden (summed up in the words given above) and of Bergmann, Karrer, Brigl and Held, and of Troensegaard are constructively analysed and their value contrasted with that of the well-known peptide hypothesis of Hofmeister. They rightly preface their review with an historical introduction in which they emphasise the momentous effect that the peptide hypothesis, as developed by Fischer, has had on the trend of protein research since the end of the last century, and they insist that new hypotheses must go further than the exemplification of possible new unions of simple amino-acids, but must be in keeping with well-established facts of protein chemistry and must help to explain the still obscure phenomena of denaturation, the extraordinary solubilities of proteins, their enormous molecular weights, and the mode of action of the proteolytic enzymes, especially of pepsin. The mass of evidence that has accumulated furnishes nearly conclusive proof that the peptide bond occurs to a very considerable extent in proteins, but the view that the protein molecule is essentially a single large polypeptide does not readily explain the phenomena mentioned above. Fischer realised that other types of combination might occur and his suggestion of the diketopiperazine ring is the origin of Abderhalden's extensive researches. Vickery and Osborne, whose criticisms and conclusions can only be briefly referred to here, admit that the sum total of the latter's evidence is impressive, but point out that he has not yet shown that any material portion of the protein molecule is thus constituted. Furthermore his synthetic products, and also those of the other investigators mentioned above, are without exception resistant to the proteolytic enzymes. Vickery and Osborne consider that the peptide hypothesis, in spite of certain shortcomings, is still the foundation stone of protein chemistry, and that advances in the near future may be looked for in the direction of an expansion of this hypothesis.

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[67] *Chem. Reviews*, 1927, **4**, 51.

[68] *Physiol. Reviews*, **1928**, **8**, **393**.

The acid–base relations of proteins, the theory of which rests on the peptide hypothesis, was summarised by Cohn in 1925.[69] From the standpoint of protein structure the most arresting publications since that date have been those of Simms.[70] On the assumption that the free groups in a protein have the same dissociation constants as they have in the simple amino-acids to which they belong, he has determined the number of equivalents of each respective grouping which must be present to give the experimental titration curve of the protein. In the case of gelatin the agreement between the number of equivalents given by the titration curve and the number of equivalents of the tervalent amino-acids known to be present from actual analysis is satisfactory except in the case of arginine. The titration curve indicates no group with a dissociation constant similar to that of the guanidine group in arginine ($pK' = 8{\cdot}1$) but instead an equivalent amount of a weak basic group ($pK' = 4{\cdot}6$). Simms suggests that in the unhydrolysed molecule this amino-acid is present in some tautomeric form, which he calls "prearginine." More recently he has studied edestin in a similar way. As before, all the arginine is present as "prearginine," and Simms further shows that this is not converted into arginine on hydrolysis with pepsin up to 18% of the total possible hydrolysis. It is of interest here to recall the fact that Schryver has repeatedly stated that the diamino-nitrogen of gelatin formed after acid hydrolysis is increased if the gelatin is first treated with cold dilute hydrochloric acid. Recently Schryver and Buston [71] claim to have shown that the increase is due partly to an increase in arginine and lysine and partly to the presence of *dl*-lysine, which has not been previously recognised as a hydrolysis product of proteins. They consider that this has not arisen by racemisation of ordinary active lysine and suggest that it is derived from some other unknown constituent of the protein. The presence of *dl*-lysine cannot explain Simms's "prearginine"—further, Simms's curves show that, if this excess of base is actually present in the unhydrolysed protein, the second amino-group must also be bound in peptide or other linkage. "Prearginine" must remain a suggestion until further chemical evidence is available.

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[69] *Physiol. Reviews*, 1925, **5**, 349.

[70] *J. Gen. Physiol.*, 1928, **11**, 629; **A.**, 837; *ibid.*, **12**, 231.

[71] *Proc. Roy. Soc.*, 1927, *B*, **101**, 519; **A.**, 1927, 785.

Another interesting fact that emerges from Simms's titration of edestin is that 50% of the extra carboxyl groups of aspartic and glutamic acids are bound in some way other than as amides, which suggests the presence of anhydrides.

Svedberg and his colleagues have found by the centrifugal sedimentation equilibrium method that the molecular weight of phycoerythrin is 208,000 ± 8000, of phycocyan 106,000 ± 5000, and of hæmocyanin $4{\cdot}93 \times 10^6$.[72] Such data are of the greatest value, for besides giving us the actual dimensions of the protein molecule they act as an independent check against methods based on chemical analysis, which can in any case only give minimum values for molecular weight.

Contributions to the problem of the structure of the protein molecule have been made by Willstätter and Waldschmidt-Leitz during the past three years, but an account of their work would be very incomplete without a discussion in some detail of their very important researches on the characterisation of the proteolytic enzymes.

Mode of Action and Specificity of the Proteolytic Enzymes.

An account of the work of Willstätter and Waldschmidt-Leitz and their collaborators on the general methods of separating and purifying enzymes was given in the Annual Report for 1926.[73] Their aim was to obtain enzymes in as pure and uniform a condition as possible, so that their action on various substrates could be studied without mutual interference. Their results during the past three years have been far-reaching, for they show that earlier workers had unwittingly used enzyme preparations that were far from homogeneous and obtained, in certain cases, results which are now shown to be invalid.

They distinguish four proteolytic enzyme types, *viz.*, pepsin, inactivated trypsin, activated trypsin, and erepsin. These have been prepared in a pure condition with respect to enzyme content, and the investigation of the specificity of their action on various substrates has contributed largely to the advances made.[74]

Erepsin.—The older preparations of this enzyme, discovered by Cohnheim and used with considerable success by Fischer and Abderhalden to split natural and synthetic polypeptides, have now been shown to be a mixture of erepsin and trypsin. Waldschmidt-Leitz [75] and his co-workers have prepared from the juice of the pancreas and from intestinal erepsin an enzyme which shows no tryptic activity, *i.e.*, it is without action on simple proteins or their higher degradation products and is capable of hydrolysing only the simplest polypeptides. The sharp difference that they were able to demonstrate between the actions of these two enzymes is well illustrated by the following table.

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[72] *J. Amer. Chem. Soc.*, 1928, **50**, 525, 1399; **A.**, 533, 783.

[73] *Ann. Reports*, 1926, **23**, 232.

[74] See Willstätter, *J.*, 1927, 1359 (Faraday Lecture); Grassmann, "Ergebnisse der Physiologie," 1928, 27.

Specificity of pancreas and intestinal proteolytic enzymes.

	Enzyme.		
	Erepsin.	Trypsin.	Trypsin + enterokinase.
Alanylglycine, glycyltyrosine, glycylglycine, glycylalanine, leucylglycine	+	—	—
Leucylglycylglycine	+	—	—
Peptone (Merck)	—	+	+ +
Clupein, Scombrin..................	—	+	+ +
Thymus-histone, casein, fibrin, gelatin, gliadin, zein	—	—	+

Until quite recently the hydrolysis of dipeptides was considered to be specific for erepsin, but Waldschmidt-Leitz [76] and his co-workers have now shown that glutamyltyrosine and phenylalanylarginine are appreciably attacked by pancreatic erepsin. The specificity of erepsin and trypsin has indeed been the subject of many papers from the laboratories of Willstätter, Abderhalden, and v. Euler during the past two years. The length of the peptide chain is not a determining factor, for the octapeptide of glycine is still attacked by erepsin.[77] The nature of the constituent amino-acids is of importance, as is shown by the fact that leucyltriglycine is attacked only by erepsin, and leucyltriglycyltyrosine only by trypsin; [77] glycyltyrosine only by erepsin and β-naphthalenesulphonylglycyltyrosine, in which the α-amino-group is substituted, only by trypsin.[78] Waldschmidt-Leitz [78] concludes that a free carboxyl group and a certain electromagnetic character of the substrate are necessary for its hydrolysis by trypsin, and that a free amino-group is necessary for erepsin. Since the amides of

[75] Waldschmidt-Leitz and Harteneck, *Z. physiol. Chem.*, 1925, **149**, 203; **A.**, 1926, 323. Waldschmidt-Leitz and Schäffner, *ibid.*, 1926, **151**, 31; **A.**, 1926, 323.

[76] Waldschmidt-Leitz, Klein, and Schäffner, *Ber.*, 1928, **61**, [*B*], 2092; **A.**, 1401.

[77] Waldschmidt-Leitz, Grassmann, and Schlatter, *Ber.*, 1927, **60**, [*B*], 1906; **A.**, 1927, 1112.

[78] Waldschmidt-Leitz, Schäffner, Schlatter, and Klein, *Ber.*, 1928, **61**, [*B*], 299; **A.**, 446.

glycine and leucine are split by erepsin, that enzyme clearly does not require the presence of a free carboxyl group.

The view that a free amino-group is necessary for the action of erepsin had already been put forward by Euler and Josephson.[79] They consider that the formation of an enzyme–peptide complex, involving the α-amino-group of the peptide, precedes hydrolysis, and conclude from experiments showing the inhibiting effect of phenylhydrazine, potassium cyanide, and sodium sulphite, all of which combine with aldehydes, that the α-amino-group attaches itself to an aldehyde group in the enzyme. Waldschmidt-Leitz and Rauchalles [80] have further developed this suggestion, and have shown that the p_H curve for the hydrolysis of glycylglycine by intestinal erepsin coincides within the limits of experimental error with that of the rate of condensation of glycylglycine with dextrose. In addition they bring forward evidence which suggests that variation of activity of the enzyme with p_H is due to the effect of the hydrogen ions on the rate of union of the enzyme and substrate, and not on the rate of decomposition. A warning, however, against the too ready acceptance of conclusions drawn from p_H activity curves is contained in a paper by Northrop and Simms.[81] Using intestinal erepsin, they have investigated the rate of hydrolysis at several different p_H values of five peptides and biuret base. The p_H activity curves differ for different substrates in a way which the authors think can be predicted on the assumption that erepsin is a weak acid or base with a dissociation constant of $10^{-7\cdot6}$, and that the action takes place between a particular ionic species of the enzyme and of the substrate. For further details the original paper, which contains much theoretical discussion, must be consulted. They conclude that the determination of the relative rates of hydrolysis of various peptides by erepsin, *i.e.*, the specificity of the enzyme, is a difficult matter except in the case where the p_H activity curves are the same for the different substrates. If this is not so, then the corrections which they consider must be applied to the observed rates are at present so speculative that the whole procedure must be regarded as very uncertain. That much of the work being done at the present time on the " specificity " of enzymes is premature is one of the conclusions to be drawn from the more recent work by Grassmann in Willstätter's laboratory on the enzymes of yeast.

Dernby [82] in 1917 showed that the proteolytic enzymes of yeast could be separated into an erepsin, a trypsin, and a pepsin. Grassmann's work suggests that the formal distinction between erepsin and trypsin may either be unnecessary, or have a different significance from that which has been assigned to it in recent years.

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[79] *Z. physiol. Chem.*, 1926, **162**, 85; **A.**, 1927, 175.

[80] *Ber.*, 1928, **61**, [*B*], 645; **A.**, 672.

[81] *J. Gen. Physiol.*, 1928, **12**, 312.

[82] *Biochem. Z.*, 1917, **81**, 107; *A.*, 1917, i, 500.

By fractional adsorption on alumina it has been found possible to separate two different homogeneous enzyme preparations, both of which appear to be specific, and both of which exhibit properties which until recently had been considered specific for "erepsin." These are (1) a dipeptidase, which will hydrolyse only dipeptides, and (2) a polypeptidase, which is inactive on dipeptides, but will hydrolyse tri- and higher peptides,[83] and even peptones.[84] The dipeptidase will not attack even a tripeptide, and is only active on those dipeptides which have a free carboxyl group in the position characteristic for normal dipeptides. Amides of dipeptides, decarboxylated dipeptides, and dipeptides in which the carboxyl group is in an unusual position, such as glycyl-β-aminobutyric acid, are unattacked. But the last compounds are all attacked by the yeast polypeptidase, which Grassmann suggests requires the presence of an amino-group, but not of a carboxyl group.[85] The action of this enzyme seems to be as specific as that of the dipeptidase. *dl*-Leucylglycylglycine is hydrolysed to *dl*-leucine and glycylglycine, and glycylglycyl-*l*-leucine gives glycine and glycyl-*l*-leucine with no trace of free leucine.[86] Such specificity at the present time is unique, and it will be interesting to observe whether Grassmann and his co-workers can separate such enzymes from other natural sources. Until it is known with some certainty that the so-called animal erepsins and trypsin, which up till now have been considered homogeneous, are not mixtures of the enzymes which it has been possible to fractionate from yeast, further work or comment on the specificity of these enzymes seems premature.

Trypsin.—The researches of Waldschmidt-Leitz and his collaborators on the specificity of the pancreatic enzymes and the unravelling of the true nature of trypsinogen and trypsin are other feats which are of great biological as well as chemical interest. Until the publication of their results the earlier view propounded by Bayliss and Starling in 1902[87] still found general acceptance. This was that trypsinogen, which was devoid of proteolytic activity, was secreted into the duodenum, in which it met with the enzyme enterokinase and was converted by this into active trypsin. Waldschmidt-Leitz has shown that this view is erroneous. Trypsinogen,

[83] Grassmann and Haag, *Z. physiol. Chem.*, 1927, **167**, 188, 202; **A.**, 1927, 794.

[84] Grassmann and Dyckerhoff, *ibid.*, 1928, **179**, 41.

[85] *Idem, Ber.*, 1928, **61**, [*B*], 656; **A.**, 672.

[86] *Idem, Z. physiol. Chem.*, 1928, **175**, 18; **A.**, 672.

[87] *J. Physiol.*, 1902, **28**, 325.

or inactivated trypsin, or simply trypsin as he prefers to call it, is itself the enzyme, and contrary to the earlier findings it possesses a specific proteolytic activity of its own. It will hydrolyse peptone and such simple proteins as clupein and scombrin, but is without action on proteins such as casein or gelatin (see Table, p. 240). Activated by enterokinase, it will attack the simple proteins much more vigorously and will act on casein and gelatin in the way that is already well known. The essential difference in the points of view is that the real enzyme trypsin is the older—so-called zymogen—trypsinogen, and that the enterokinase is not an enzyme as was formerly supposed, but merely an activator of the trypsin. This important result has been reached by applying Willstätter's adsorption methods to the purification of the enzymes of the pancreas.

An extract of dried pancreas contains erepsin, trypsin, and trypsin-kinase. To this extract a solution of caseinogen is added.[88] On precipitating the protein with acetic acid the trypsin-kinase is specifically adsorbed, and is removed by filtration. This operation is twice repeated to ensure complete removal of the trypsin-kinase. The filtrate, containing the trypsin and erepsin, is then treated with kaolin. Trypsin is more basic and is preferentially adsorbed, and by repeating the process a sufficient number of times homogeneous preparations of the two enzymes can be obtained.[89] Enterokinase free from erepsin can be prepared by precipitating it first with acetic acid, then with mercuric chloride, and decomposing the latter precipitate with hydrogen sulphide.[90] It cannot be prepared by adsorption with kaolin or caseinogen, as the specific trypsin-binding group of the activator is taken up by the protein. Using homogeneous enzyme preparations separated in this way, Waldschmidt-Leitz has been able to demonstrate their respective specificities outlined above. Further experiments have shown that the enzyme activity of pancreatic juice is only one-fifth that of the extract of the gland,[91] so for experimental purposes the dried gland is more useful than the natural secretion.

Using caseinogen as a substrate, Waldschmidt-Leitz and Shinoda [92] have investigated the hydrolytic action of erepsin-free trypsin from three different animal sources, activated with erepsin-free enterokinase from eleven different animal sources. With trypsin from the pig and cat, the activation was the same in all cases; with sea-lion trypsin, the activation was very similar except with the enterokinases from the pig and ox. The difference in the activity of trypsin and trypsin-kinase (trypsin + enterokinase) is not yet understood. Both enzymes can be adsorbed on aluminium hydroxide or caseinogen without loss of activity or specificity, but enterokinase itself is thereby inactivated. Clearly the enterokinase portion of the trypsin-kinase molecule which is responsible for the difference in the specificity of the two enzymes is not concerned directly in the adsorption linkage.[93] The magnitude of this difference is well illustrated by the following experiment, using as substrates four of the protamines which have been analysed by Kossel.[94] The first two columns show the relative amount of hydrolysis with the two enzymes, and the third the relative proline content of the proteins,

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[88] Waldschmidt-Leitz and Linderström-Lang, *Z. physiol. Chem.*, 1927, **166**, 241; **A.**, 1927, 698.

[89] Waldschmidt-Leitz and Harteneck, *ibid.*, 1925, **147**, 286; *A.*, 1925, i, 1361.

[90] Waldschmidt-Leitz and Künstner, *ibid.*, 1927, **171**, 290; **A.**, 1928, 550; Waldschmidt-Leitz, *ibid.*, 1925, **142**, 215; *A.*, 1925, i, 741.

[91] Waldschmidt-Leitz and Waldschmidt-Graser, *ibid.*, 1927, **166**, 247; **A.**, 1927, 698.

[92] *Ibid.*, 1928, **176**, 301; **A.**, 922.

	Enzyme.		
	Trypsin.	Trypsin-kinase.	Relative proline content.
Clupeine	0·90	3·10	4
Salmine	1·00	3·18	3
Scombrine	0·60	2·96	2
Sturine	0·02	3·95	-

which shows a rough correlation with tryptic activity. The other constituent amino-acids, chiefly arginine, show no correlation at all.

Pepsin.—Very active, ash-free preparations of pepsin have recently been made by F. Fenger, R. H. Andrew, and A. W. Ralston,[95] who precipitate the enzyme at p_H 2·5. Analysis shows that it is a protein containing a very high proportion of monoamino-acids, some sulphur and phosphorus, but no halogen. It is doubtful, however, if a neater or more rapid method of purification or concentration is required than the safranine method originally devised by Marston [96] and perfected by Forbes.[97] The enzyme is quantitatively precipitated by the safranine, and can be recovered by dissolving the precipitate in 20% alcohol, containing a little oxalic acid, and extracting the dye with butyl alcohol. Preparations with twenty times the original activity can be made in this way. Newer methods of determining peptic activity, depending on a new choice of indicator or dye adsorbed on the substrate, have been published by Linderström-Lang,[98] Beer and Peczenik,[99] Citron,[1] and Kawahara and Peczenik.[2]

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[93] Waldschmidt-Leitz and Linderström-Lang, *Z. physiol. Chem.*, 1927, **166**, 227; **A.**, 1927, 698.

[94] Waldschmidt-Leitz and Kollmann, *ibid.*, p. 261; **A.**, 1927, 698.

[95] *J. Biol. Chem.*, 1928, **80**, 187.

[96] *Biochem. J.*, 1923, **17**, 851; *A.*, 1924, i, 350.

[97] *J. Biol. Chem.*, 1927, **71**, 559; **A.**, 1927, 378.

That the apparent specific action of pepsin is of a different type from that of trypsin or erepsin—in which the action is confined to the hydrolysis of the peptide linkages with the formation of carboxyl and amino-groups—has been noted since the early days of formol titration. Although proteins are changed very materially by the action of pepsin, the increase of formol titration is relatively very small, which suggests that its action is more complex than simple peptide splitting. Confirmation of this is found in the fact that synthetic polypeptides are, without exception, unattacked by it. Steudel [3] and his co-workers in 1926 published results which seemed to show that in peptic digestion the increase of acid groups (measured by Willstätter's method) was greater than that of the basic groups (measured by Van Slyke's method). Opposed to this finding were those of Waldschmidt-Leitz and Simons,[4] who showed that in the peptic digestion of casein, egg albumin, and ricinus globulin the ratio of the increases was unity; although they found that other proteins, such as zein and gelatin, behaved irregularly. Felix and Harteneck [5] found the ratio for thymus histone was unity, as also did Weber and Gesenius [6] for casein. Sörensen and Katschioni-Walther [7] have made a critical study of the methods of analysis, and have reinvestigated the problem, using casein, gliadin, and gelatin as substrates. Using Willstätter's method for estimating the acid groups and Linderström-Lang's method for basic groups, they find that the ratio of the increases on peptic hydrolysis is unity and ascribe the earlier conflicting results to faulty methods of technique. Waldschmidt-Leitz and Künstner [8] published at the same time similar results, and as the basic groups had been estimated by Van Slyke's method there is no doubt that the increase is due to liberation of free amino-groups. They conclude that peptic hydrolysis is confined to the peptide bond, and that the extent of such hydrolysis bears a definite and simple ratio to the extent of the hydrolysis by trypsin and erepsin. Sörensen, whilst agreeing that such a conclusion would be of great importance from the point of view of protein structure, considers that on present published evidence it is somewhat premature.

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[98] *Z. physiol. Chem.*, 1928, **174**, 251; **A.**, 551.

[99] *Fermentforsch.*, 1928, **10**, 88.

[1] *Deut. Med. Woch.*, 1926, **52**, 1781; **A.**, 1927, 372.

[2] *Wien Med. Woch.*, 1926, **72**, 129; **A.**, 1927, 372.

[3] Steudel, Ellinghaus, and Gottschalk, *Z. physiol. Chem.*, 1926, **154**, 21, 198; **A.**, 1926, 866; Steudel and Ellinghaus, *ibid.*, 1927, **166**, 84; **A.**, 1927, 698.

[4] *Z. physiol. Chem.*, 1926, **156**, 114; **A.**, 1926, 1060.

[5] *Ibid.*, 1927, **165**, 103; **A.**, 1927, 477.

[6] *Biochem. Z.*, 1927, **187**, 429; **A.**, 1927, 992.

[7] *Z. physiol. Chem.*, 1928, **174**, 251; **A.**, 551; *Compt. rend. Trav. Lab. Carlsberg*, 1928, 17, No. 7.

[8] *Z. physiol. Chem.*, 1927, **171**, 70; **A.**, 1928, 550.

The above account of the proteolytic enzymes shows what powerful weapons Waldschmidt-Leitz and his colleagues are slowly forging. Their work is still incomplete, and it is probable that we do not yet understand the true specificity of these enzymes. If Waldschmidt-Leitz and his colleagues can, finally, unravel the mystery of peptic digestion, they will have made the greatest contribution to the problem of protein structure since the peptide hypothesis of Hofmeister and Fischer.

Carbohydrate Phosphoric Acid Esters.

The Carbohydrate Phosphoric Acids of Yeast Fermentation.—In the Report of last year reference was made to the important work of Morgan and Robison on the constitution of the hexosediphosphoric acid of yeast fermentation, work which led them to the suggestion that this important intermediary substance was γ-fructose-1 : 6-diphosphoric acid.[9] Full details of this work are now available [10] and whilst it is not necessary to refer further to this important advance in the present Report, it is significant that the suggestions made by Morgan and Robison are strongly supported in a recent publication by Levene and Raymond.[11] These workers show that the rate of acid hydrolysis of the methylfructosidic derivative of hexosediphosphoric acid is that of a butylene-oxidic (γ-) fructose compound (<2,5>lactal structure in Levene's nomenclature). It follows that the more stable phosphoric acid residue must be in position 6, and the structure finally deduced for the parent hexosephosphoric acid is the same as that assigned to it by Morgan and Robison. Levene and Raymond are also in agreement with the suggestion that Neuberg's monophosphoric acid, derived from the diphosphoric acid by hydrolytic removal of the more labile phosphoric acid group, is γ-fructose-6-monophosphoric acid.

In the past year considerable progress has been made in the study of the various hexosemonophosphoric acids of biological origin. There is now little room for doubt that previous conflicting results recorded in efforts to elucidate the nature of the hexosemonophosphoric acid, formed along with the diphosphoric acid in yeast fermentations, are to be ascribed to the presence in this material of different monophosphates, an observation which would also seem to apply to the monophosphoric acid of muscle. One of the most significant advances which falls to be recorded in this field is the isolation by Robison and Morgan [12] of trehalosemonophosphoric acid in the course of their studies of the " monophosphate " fraction of the phosphoric acid esters of sugars formed by yeast. It will probably be convenient to remind the reader that the diphosphoric acid can be separated readily from the monophosphoric acid in virtue of the much greater solubility of the barium salt of the latter, as compared with that of the former acid. It is in the more soluble barium salt fraction that the interesting new disaccharide monophosphoric acid is found. Trehalose is a rare non-reducing disaccharide found in the "manna" excreted by the insect *Larinus maculatus,* in certain fungi, seaweeds, and yeast. It has the constitution :

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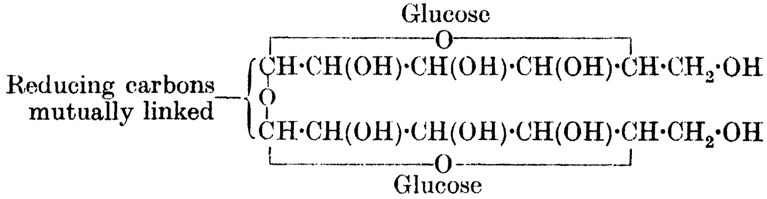
[9] *Ann. Reports*, 1927, **24**, 252. [10] *Biochem. J.*, 1928, **22**, 1270; **A.**, 1213.
[11] *J. Biol. Chem.*, 1928, **80**, 633.



$$\begin{array}{l} \overbrace{\text{CH·CH(OH)·CH(OH)·CH(OH)·CH}}^{\text{O}}\text{·CH}_2\text{·OH} \\ \text{O} \\ \underbrace{\text{CH·CH(OH)·CH(OH)·CH(OH)·CH}}_{\text{O}}\text{·CH}_2\text{·OH} \end{array}$$

The new sugar ester is formed when glucose or fructose is fermented with dried yeast or zymin. Under these conditions it comprises some 10—20% of the total phosphoric acid in ester combination, the remaining 80—90% being the typical hexosediphosphoric acid. On the other hand, by varying the conditions of the fermentation considerable alterations can be made in the nature of the carbohydrate phosphoric acid esters produced and it would appear that trehalosemonophosphoric acid is not an obligate product. For instance, when yeast juice is used as the fermentative agent the diphosphoric acid fraction is less than half of the total esterified phosphorus, and trehalosemonophosphoric acid is not found in the typical monophosphoric acid fraction, which would appear to consist entirely of monosaccharide esters. Similar variations in the balance between diphosphoric and monophosphoric acid fractions have been noted by Kluyver and Struyk [13] in making use of different samples of yeast in the presence of phosphates. Thus in fermentations in which there occurs a rapid rise to maximum velocity, followed by a fairly rapid fall to the initial rate, there is found a large proportion of the diphosphoric acid, whilst in other cases in which the increased fermentation, following the addition of phosphate, is less marked and of longer duration, almost the whole of the esterified phosphorus is present as the monophosphoric acid.

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[12] *Biochem. J.*, 1928, **22**, 1277; **A.**, 1285.

[13] *Proc. K. Akad. Wetensch. Amsterdam,* 1927, **30**, 871; **A.**, 1928, 398.

Trehalosemonophosphoric acid has $[\alpha]_{5461}$ + 185° for the free acid, + 132° for the barium salt, and + 31° for the brucine salt. It is readily dephosphated by the action of bone phosphatase and pure crystalline trehalose (m. p. 96—98°; $[\alpha]_{5461}$ + 222°) is subsequently isolated. The ester is fermented readily by dried yeast and more slowly by yeast juice and zymin. It is not yet possible to state what significance this interesting new phosphoric ester may have in yeast fermentations, but, as Robison and Morgan suggest, it is by no means impossible that the introduction of the phosphoric acid group may facilitate the building up of complex reserve carbohydrates from the simple sugars. That trehalosemonophosphoric acid is formed by some active fermentation process is proved by the observation that in the dried yeast used in the fermentations neither free trehalose nor its monophosphoric ester was found in quantities sufficient to account for the amount of the latter isolated from the fermentation products. It is not yet possible to express an opinion on the identity or otherwise of the new trehalosemonophosphoric acid with a synthetic product described some years ago by Helferich, Löwa, Nippe, and Riedel [14] as resulting from the action of phosphoryl chloride on trehalose in pyridine solution. It had the composition of a monophosphate and its barium salt had $[\alpha]_D$ + 135·5°, somewhat lower than the corresponding value for the barium salt of Robison and Morgan's compound.

During the past year there has been recorded the preparation of another disaccharide monophosphoric acid by biological means. Neuberg and Leibowitz [15] found that the action of the lactic acid bacterium, *B. Delbrücki*, on sodium hexosediphosphoric acid of yeast resulted in a partial dephosphatisation and gave, in 30% yield, a *reducing* disaccharide monophosphoric acid, the barium salt of which had $[\alpha]_D$ + 38° and the free acid + 57°. Clearly this acid differs materially from Robison and Morgan's trehalose ester, but the synthetic analogy is an interesting one.

Eüler, Myrback, and Runehjelm [16] confirm the observation that fermentation of glucose by means of dried yeast yields, after separation of the diphosphoric acid as the sparingly soluble barium salt, a monophosphoric acid fraction identical with that first described by Robison, and further claim to have isolated a new hexosemonophosphoric acid by fermenting glucose with very active yeast. The new acid has $[\alpha]_D$ + 63° and its barium salt $[\alpha]_D$ + 33°, values which are much higher than those recorded for Robison's monophosphoric acid. The possibility of this new acid being contaminated with compounds of the type of the new trehalose mono-ester, which possesses a remarkably high rotation, should not yet be excluded. From their studies of the mono- and di-phosphoric acid fractions Eüler and Myrback[17] conclude that the course of fermentation of glucose by yeast in the presence of phosphates proceeds in the following stages : (1) synthesis of Robison's monophosphoric acid, (2) conversion of the mono-ester under the action of a mutase and a co-zymase into alcohol and carbon dioxide and into the diphosphoric acid, (3) conversion of the diphosphoric acid by the action of a phosphatase into a hexose, presumably fructose, and (4) the participation of the hexose in the chain of reactions at (1).

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[14] *Z. physiol. Chem.*, 1923, **128**, 141; *A.*, 1923, i, 898.

[15] *Biochem. Z.*, 1928, **193**, 237; **A.**, 447.

[16] *Arkiv Kemi. Min., Geol.*, 1928, **9**, 1; **A.**, 1158.

It is well established from the data reviewed in the foregoing and from those previously available, that by securing appropriate conditions of fermentation, yeast may form at least four carbohydrate phosphoric acid esters, namely, a fructosediphosphoric acid, and three monophosphoric acids, those of trehalose, of an aldose (probably glucose), and of a ketose (possibly fructose). The mixture of the two last-mentioned comprises Robison's acid.

The Hexosemonophosphoric Acid of Muscle.—It is not altogether unexpected to find that *pari passu* with the development of our views on the phosphoric acid metabolism of the yeast cell, equally striking complexities are brought to light in the investigation of the carbohydrate phosphoric acid esters of the muscle. It is now well known that by using the fluoride–glycogen fermentative resynthesis, it is possible to obtain from mammalian muscle pulp a hexosediphosphoric acid identical with that formed by the yeast cell. On the other hand, the normally occurring hexosephosphoric ester of muscle is a monophosphate.[18] The latter has been investigated by Pryde and Waters,[19] who obtained from the muscles of rabbits, goats, and a donkey, preparations which were apparently identical with one another and consisted of some 90% of an aldose component as determined by a comparison of the copper reduction value with the Willstätter–Schudel hypoiodite figure. This result is in close accord with that of Embden and Zimmermann.[20] Pryde and Waters have subjected the monophosphoric acid to bromine oxidation, followed by dephosphatisation, using aqueous hydrobromic acid under pressure. The product eventually obtained had the properties of gluconic acid, and they conclude that some 90% of the muscle monophosphoric acid is derived from glucose. The remaining 10%

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[17] *Annalen*, 1928, **464**, 56; **A.**, 1053. [18] *Ann. Reports*, 1927, **24**, 255.

[19] Report of the Meeting of the Biochemical Society (Dec. 14th), *J. Soc. Chem. Ind.*, 1928, **47**, 1346.

[20] *Z. physiol. Chem.*, 1927, **167**, 114; **A.**, 1927, 749.

is presumably a ketose monophosphate, but further investigation is necessary before its identity can be considered as established. A comparison of the rotations of the free acids and barium salts prepared from purified yeast and muscle monophosphoric acid fractions suggests that these, if not identical, are constituted on very similar lines. This view is supported by Lohmann,[21] who shows that the kinetics of hydrolysis of the muscle monophosphoric acid and Robison's yeast acid follows the same course. It is none the less clear that great care is necessary in interpreting such results in view of the obviously mixed nature of the products obtained both from yeast and from muscle. Modifications in the method of isolation may lead to changes in the relative amounts of the two components, and although the presence of a disaccharide ester in the products of the muscle process has not so far been demonstrated, the isolation from yeast fermentations of trehalosemonophosphoric acid, possessing some of the physical properties of the monosaccharide monophosphoric acids (*e.g.*, solubility of the barium salt), is a clear indication of the caution necessary in such investigations.

Pyrophosphate in Muscle.

An observation of the greatest importance has been made by Lohmann,[22] who finds that a considerable part of the increased inorganic phosphate observed when muscle pulp is digested with sodium bicarbonate solution is due to the enzymic hydrolysis of a *pyro*phosphate to the normal *ortho*phosphate. Thus it is found that in the fresh muscle of the frog or rabbit some 0·6 to 0·7 mg. per cent. of P_2O_5 (or one-fifth of the total acid-soluble phosphate) is present as pyrophosphate and is completely hydrolysed to orthophosphate by an alkaline muscle extract at 40—50°. The muscle pyrophosphate has been precipitated as the copper salt from a trichloroacetic acid extract of muscle and identified as the crystalline sodium salt and as the tetramminocobaltipyrophosphate ($+2H_2O$). Since artificially prepared pyrophosphates obtained from alkali biphosphates also show this hydrolysis, and since muscle pulp when heated for one minute on the water-bath loses its power to hydrolyse pyrophosphate, it is inferred that the process is an enzymic one. The muscle pyrophosphate would appear to undergo hydrolysis in rigor. The process is not related to the production of lactic acid in the intact muscle and it may occur in carbohydrate-free media. Further details of this extremely interesting discovery will be eagerly awaited. Obviously, if it be substantiated, much careful reconsideration will have to be given to all previous work in which the breakdown of lactacidogen in muscle is estimated in terms of inorganic phosphoric acid liberated. Although at first sight the enzymic hydrolysis of a typically inorganic product such as a mineral pyrophosphate seems remarkable, there is already a suggestive analogy, in that Kitasato [23] has shown, with appropriate controls, that sodium hexametaphosphate, $(NaPO_3)_6$, is hydrolysed by taka-phosphatase and by the phosphatases of rabbit liver and kidney, and of yeast, to yield orthophosphate. More recently, in a detailed study of the range of action of phosphatases, Neuberg and Jacobsohn [24] show that the dipotassium salts of di-*o*-cresol, di-*m*-cresol, and di-α-naphthol pyrophosphoric acids, that is, compounds of the type

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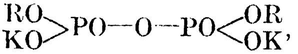
[21] *Biochem. Z.*, 1928, **194**, 306; **A.**, 665.

[22] *Naturwiss.*, 1928, **16**, 298; **A.**, 1054.



$$\begin{matrix}RO\\KO\end{matrix}\!>\!PO{-}O{-}PO\!<\!\begin{matrix}OR\\OK\end{matrix},$$

where R signifies the organic radical, are hydrolysable by various phosphatases with the production of orthophosphoric acid. For example, the *o*-cresol derivative showed in thirteen days 90% hydrolysis with a liver phosphatase, 77% with kidney phosphatase, and 4·4% with muscle phosphatase. One may therefore infer that all types of phosphoric acid, ortho, meta, and pyro, in organic combination may be susceptible to enzymic hydrolysis, and further that inorganic meta- and pyro-phosphates may undergo a similar change, all with the production of orthophosphoric acid. The observations briefly reviewed here suggest a remarkable extension of our already comprehensive views regarding the biological rôle of phosphoric acid.

Lactic Acid Formation in Muscle.—The observations discussed in the preceding paragraph obviously have an important bearing on three very well documented studies of the enzymic formation of lactic acid in muscle and the relationship of phosphoric acid to this process. These comprise two contributions by Stiven [25] and one by Beattie, Bell, and Milroy.[26] Stiven infers from his results that phosphoric ester accumulation is not an essential accompaniment of lactic acid formation from glycogen. When ester accumulation does occur, there is no definite constant ratio of the molar amount of lactic acid produced to the amount of phosphoric acid that accumulates as ester. In the second period of muscle activity, when the ester accumulated in the first period is broken down, the molar ratio of lactic acid produced to phosphoric acid set free is also very variable. Beattie, Bell, and Milroy show that when extracts of muscle are incubated at 22° to 45° in bicarbonate solution there is,

[23] *Biochem. Z.*, 1928, **187**, 257; **A.**, 1282.

[24] *Ibid.*, 1928, **199**, 498.

[25] *Biochem. J.*, 1928, **22**, 867, 874; **A.**, 796.

[26] *J. Physiol.*, 1928, **65**, 109; **A.**, 921.

approximately, an equimolar production of phosphoric and lactic acids. When glycogen is added, formation of lactic acid and esterification of phosphoric acid occur in roughly equimolar proportion. It is admittedly difficult to weld into a coherent scheme these diverse results and obviously with the rapid accumulation of information concerning the nature and reactivities of the various phosphoric acid compounds present in muscle it would be unwise to attempt the task at the present juncture.

In last year's Report [27] detailed reference was made to the important work of Meyerhof on the separation of the lactic acid ferment from muscle. An extension of this work has been presented by Meyer,[28] who describes in detail methods of purifying the lactic acid-forming enzyme leading to the isolation of preparations 20 to 50 times as active as the original material.

Boyland [29] has collected interesting data regarding the formation of lactic acid in invertebrate muscle and in vertebrate cardiac muscle. He finds that the change of glycogen into lactic acid accompanies activity in invertebrate muscle in the same way as in the muscle of vertebrate animals. At the same time the muscles of crustaceæ, lamellibranchs, and gastropods appear to act as stores of glycogen, and in the last two instances there are found large quantities of glycogen which cannot be converted into lactic acid by the muscle under known optical conditions for this change. The heart muscle of invertebrates differs from that of vertebrate animals in not producing less lactic acid than the skeletal muscle of the same animal, and in not producing lactic acid in excess of the glycogen present. It is suggested that the excess production of lactic acid in vertebrate cardiac muscle may possibly be derived from the inositol of the muscle.

Phosphagens.

The interesting discovery of the existence in muscle of a labile form of nitrogenous organic compound of phosphoric acid (phosphagen), to which reference was made in the Report of last year,[30] has led to numerous investigations and further important advances. Irving and Wells [31] have detected the presence of labile phosphorus compounds of the type of phosphagen in the voluntary muscles of all vertebrates examined by them with the exception of fishes. They were unable to detect labile phosphoric acid in the smooth muscle of either vertebrates or invertebrates or in heart muscle. In a general way these workers therefore substantiate the parallelism previously observed between the distribution of labile phosphoric acid and creatine. Martino[32] records that, on comparing the muscles of the rabbit and pigeon, he found that those capable of contracting more rapidly contained more phosphagen and less inorganic phosphoric acid. In regard to this question two further recently published studies merit attention. Ferdmann and Feinschmidt[33] show that white muscle of the rabbit and fowl contains more creatinephosphoric acid than mixed or red muscle. In white muscle the phosphagen accounts for 30% of the total creatine, but this percentage is much less in the case of red muscle. These workers find traces of the substance in smooth muscle; it is also said to be present in the spleen, testes, uterus, stomach, and heart but is absent from the kidney. Palladin and Epelbaum[34] find that the white muscle (biceps femoris) of the guinea-pig is richer in creatinephosphoric acid, creatine, and lactacidogen than the red muscle (M. semitendinosus). The latter workers corroborate the statement of Ferdmann and Feinschmidt regarding the higher percentage of combined creatine in white muscle as compared with red muscle.

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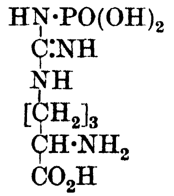
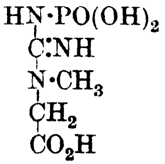
[27] *Ann. Reports*, 1927, **24**, 258.
[28] *Biochem. Z.*, 1928, **193**, 139; **A.**, 444.
[29] *Biochem. J.*, 1928, **22**, 362; **A.**, 545.
[30] *Ann. Reports*, 1927, **24**, 256.
[31] *J. Biol. Chem.*, 1928, **77**, 97; **A.**, 665.

In a series of papers by Meyerhof and Lohmann[35] the study of phosphagen is materially advanced. In the first place, in addition to the original phosphagen (creatinephosphoric acid) a new guanidinophosphoric acid (the generic name suggested by Meyerhof for phosphagens) has been isolated. This is argininephosphoric acid and it appears to participate in the chemical mechanisms of crustacean muscle in a manner similar to that of creatinephosphoric acid in vertebrate muscle. The barium salt of the new phosphagen has $[\alpha]_D + 2°$ and the free acid $[\alpha]_D + 5°$. It possesses a free α-amino-group, but it is not attacked by arginase. It is split into arginine and phosphoric acid on contraction of the muscle and is resynthesised during the aerobic recovery phase. The two phosphagens so far discovered are formulated as follows:



$$\begin{array}{l} \mathrm{HN{\cdot}PO(OH)_2} \\ \;\mathrm{C{:}NH} \\ \;\mathrm{NH} \\ \mathrm{[CH_2]_3} \\ \;\mathrm{CH{\cdot}NH_2} \\ \;\mathrm{CO_2H} \end{array}$$

Argininephosphoric acid.



$$\begin{array}{l} \mathrm{HN{\cdot}PO(OH)_2} \\ \;\mathrm{C{:}NH} \\ \;\mathrm{N{\cdot}CH_3} \\ \;\mathrm{CH_2} \\ \;\mathrm{CO_2H} \end{array}$$

Creatinephosphoric acid.

The two more important papers from the Meyerhof laboratory, already referred to in the foregoing, deal with the physico-chemical properties and physiological behaviour of the two phosphagens. It is shown that the enzymatic hydrolysis of creatinephosphoric acid in a muscle extract is adversely affected by carbohydrate and inhibited by fluoride. The rate of hydrolysis is dependent on the p_H of the extract and has an optimum between p_H 6·4 and 7·0. In fresh muscle extracts more alkaline than p_H 8·0 a synthesis of the phosphagen occurs. The synthetic effect is increased by the addition of creatine. Argininephosphoric acid shows a similar behaviour in a qualitative sense, but, even at the neutral point, its tendency to be synthesised in the muscle extract is predominant and is maximal at p_H 8·0. Monoaminophosphoric acid, like the two phosphagens, is hydrolysed by muscle extract, a hydrolysis which is also inhibited by fluoride. The heats of hydrolysis and the dissociation curves of the two natural phosphagens and of aminophosphoric acid have been carefully measured by Meyerhof and Lohmann [36] at acid and neutral reactions. It is shown that the hydrolysis of the phosphagens in the muscle in the vicinity of the neutral point involves hardly any alteration of the p_H and thus there is formed a strong buffer system from a system previously devoid of buffering power.

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[32] *Atti R. Accad. Lincei*, 1928, **7**, 79; **A.**, 546.

[33] *Z. physiol. Chem.*, 1928, **178**, 173; **A.**, 1393. [34] *Ibid.*, p. 178; **A.**, 1393.

[35] *Naturwiss.*, 1928, **16**, 47; **A.**, 1277; *Biochem. Z.*, 1928, **195**, 22, 49; **A.**, 917.

A further publication from Meyerhof's laboratory [37] deals with the decomposition of creatinephosphoric acid in muscular activity and compares the extent of hydrolysis of the phosphagen with the lactic acid formation and with the tension developed in the muscle. In tetanus the hydrolysis of the phosphagen is the same for direct as for indirect stimulation, but is markedly diminished in curarised muscle, whereas the lactic acid formation is the same under all three sets of conditions and varies only with the severity of tetanus. In addition to the aerobic resynthesis of creatinephosphoric acid first described by Eggleton and Eggleton,[38] Nachmansohn shows that an anaerobic resynthesis occurs immediately after relaxation, that this process is complete in about 20 seconds, and that it involves a resynthesis of some 30% of the hydrolysed phosphagen. During this anaerobic resynthesis no lactic acid is formed, nor does any muscle ammonia disappear, and it is concluded that the whole question of ammonia formation in muscle is not related to the presence of creatinephosphoric acid. The anaerobic resynthesis has also been studied by Gorodissky [39] in the isolated frog's muscle. In the first place, this worker confirms the observation of Eggleton and Eggleton [40] that short-period tetanic stimulation of the isolated frog's gastrocnemius muscle decreases the creatinephosphoric acid and that this phase is followed during aerobic recovery by a resynthesis. After stimulation of longer duration (12 seconds) it is observed that resynthesis may occur anaerobically. Gorodissky does, however, find that resynthesis occurs more readily in the presence than in the absence of oxygen, and after prolonged stimulation (25 seconds) it is only observed to occur under aerobic conditions.

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[36] *Loc. cit.* [37] Nachmansohn, *Biochem. Z.*, 1928, **195**, 75; **A.**, 917.

[38] *Ann. Reports*, 1927, **24**, 256.

[39] *Z. physiol. Chem.*, 1928, **175**, 261; **A.**, 917. [40] *Loc. cit.*

Further observations on the physiological behaviour of phosphagen are contributed by Eggleton and Eggleton.[41] They find that the rate of disappearance of creatinephosphoric acid from a resting muscle under anaerobiosis is much higher than the rate of lactic acid production. The decomposition of phosphagen in fatigue, rigor, or incubation in bicarbonate solutions, produces free creatine in amount corresponding to the creatinephosphoric acid which has disappeared. After being fatigued and subsequently exposed to oxygen, the muscle resynthesises phosphagen very rapidly, this process being much more rapid than the corresponding resynthesis of glycogen from lactic acid. Under resting anaerobic conditions the phosphagen lost by the muscle is completely accounted for by the inorganic phosphoric acid produced, but in activity part of the phosphoric acid enters into organic ester combination. When the muscle is incubated in the presence of sodium fluoride, all the phosphoric acid is converted into the organic ester form. Eggleton and Eggleton are of the opinion that the phosphate radical of phosphagen is made use of by the muscle, when stimulated to activity or when incubated in the presence of fluoride, to esterify some organic compound. In reference to this question one may mention here that Ferdmann [42] has found that, for the formation of lactacidogen *in vitro* from the inorganic phosphoric acid of muscle pulp, the presence of creatinephosphoric acid is not necessary. It would seem that incubation in the presence of fluoride must lead to the formation of fructosediphosphoric acid, first isolated from muscle by Embden and Zimmermann,[43] and since this compound has not been detected in fresh muscle untreated with fluoride, it does not appear that the esters formed under conditions of normal activity and under the influence of fluoride can be the same. None the less Eggleton and Eggleton conclude that the phosphoric ester produced in activity, and whose formation is deduced from an increased acid-soluble organic phosphorus figure, is the same as Embden's lactacidogen, since the former is rapidly hydrolysed by the muscle enzymes when the chopped muscle is incubated in a bicarbonate buffer. As these are the conditions under which pyrophosphate is stated to be hydrolysed in muscle extracts, one hesitates to stress this question of the identity of the ester formed in activity with lactacidogen. The muscle processes appear to be of such a complex nature that at present it seems unwise to raise a too elaborate superstructure of theory on data amassed purely by methods of analysis carried out in what are admittedly complex media.

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[41] *J. Physiol.*, 1928, **65**, 15; **A.**, 546.

[42] *Z. physiol. Chem.*, 1928, **178**, 52; **A.**, 1267.

[43] *Ann. Reports*, 1927, **24**, 255.

From these observations which have been reviewed in some detail there can now be no doubt that the reversible decomposition of creatine- or arginine-phosphoric acid is an integral part of the muscle activity, but as yet our knowledge is too fragmentary to warrant any statement concerning the exact function of these phosphagens. One of the most recent suggestions advanced by Meyerhof and Nachmansohn [44] is that phosphagen is decomposed wholly or at least principally during excitation rather than during contraction of the muscle. It is shown that when the nerves are paralysed by tetramethylammonium chloride the decomposition is greatly hindered, and resynthesis is rapid and complete on relaxation. Furthermore an indirect confirmation of the association between creatinephosphoric acid and excitation is afforded by the observation that the excitability and phosphagen concentration of a muscle are both increased by suspending the muscle in an inorganic phosphate solution of higher concentration than that present in the muscle itself.

Ammonia Formation in Muscle.

During the past year much attention has been given to the question of the traumatic or functional formation of ammonia in muscle, a phenomenon first observed by Parnas and Mozolowski.[45] A lengthy and important series of papers [46] dealing with the question of ammonia formation in muscle and of the relationship of adenylic acid to this process has just appeared from Embden's laboratory. These carry the question much further than the results of any previous investigator, but for the reason stated below [47] they must be reserved for review in a subsequent Report. Suggestive but somewhat inconclusive experiments have been carried out by Rösch and Kamp,[48] who show that when the retina of the frog is exposed to light a marked increase in ammonia occurs. Fresh ox retina pulp kept in 2% sodium bicarbonate solution at 40° gives rise to the formation of ammonia by an enzymic process which is rapid and complete in less than two hours. The addition of guanylic acid to such retina pulps does not cause any notable increase in the ammonia production, but on the other hand the addition of adenylic acid produces a marked increase, representing in some cases a yield of 90% of the amino-group present in this acid. It is, however, suggested that the evidence is against the precursor of ammonia being adenylic acid, at least in the retina, since, after the pulp has been treated with 1% hydrochloric acid, treatment which destroys the ammonia-producing enzyme, no ammonia formation can be detected on addition of an extract of muscle which has a powerful deaminising action on adenylic acid. None the less, despite these inconclusive results obtained with the retina, the balance of the evidence at present available strongly suggests that adenylic acid is the ammonia precursor of muscle, and indeed the new results from Embden's laboratory would seem to prove this.

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[44] *Naturwiss.*, 1928, **16**, 726; **A.**, 1277. [45] *Ann. Reports*, 1927, **24**, 257.

[46] *Z. physiol. Chem.*, 1928, **179**, parts 4, 5, and 6.

[47] The papers, which are seven in number and occupy 162 pages of the journal, appeared after this Report had been drafted. The Reporter has therefore judged it advisable to reserve this important work for a subsequent Report rather than to incorporate it with undue brevity in the present Report.

[48] *Z. physiol. Chem.*, 1928, **175**, 158; **A.**, 792.

That the ammonia formation in the muscle is subject to nervous influence is shown by Büttner.[49] He finds that the traumatic formation of ammonia in frog's muscle after section of the sympathetic nerves is some 50% higher than in the corresponding muscles with the sympathetic nerve supply left intact. When the denervated muscle is stimulated electrically, the ammonia formation may be 60% higher than in the control muscle. On the other hand, the resting ammonia value is not regularly influenced by sympathectomy. Mozolowski and Lewinski [50] find that the formation of ammonia in frog's muscle is much higher in summer than in winter and presumably therefore bears some relationship to the metabolic state of the animal. In the muscles of the intact normal frog the ammonia accumulated during work slowly decreases and the resting value is strongly affected by the animal's movements. The ammonia content of nervous tissue, unlike that of muscle tissue, is not affected by pulping. In the curarised animal, stimulation of the nerves yields no increase in the ammonia of the muscle, but direct stimulation gives the same effect as in the non-curarised animal. Sodium fluoride diminishes ammonia formation in muscle pulp, but it is without effect on the fresh, excised muscle, which shows, with the onset of paralysis, the same ammonia formation as is produced by trauma, or heat or caffeine rigor.

Chrząszczewski and Mozolowski [51] have studied the course of traumatic formation of lactic acid and ammonia in pulped muscle and find certain parallelisms. Thus when a muscle is macerated with sand and water the lactic acid formed in two minutes is ten times the resting value and the course of formation is similar to that of ammonia. A borate solution of p_H 9·3 inhibits both traumatic lactic acid and ammonia formation in the same manner. But since sodium fluoride entirely abolishes lactic acid formation and only more or less diminishes the ammonia formation, it is concluded that the two traumatic processes are not directly related to one another.

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[49] *Biochem. Z.*, 1928, **198**, 478; **A.**, 1277.

[50] *Ibid.*, 1928, **190**, 388; **A.**, 198.

[51] *Ibid.*, 1928, **194**, 233; **A.**, 668.

Carbohydrate Metabolism of Pathological Overgrowths.

During the past few years Warburg and his co-workers have devoted considerable attention to the mechanism of utilisation of carbohydrates by cancerous growths. Most of the numerous papers which have appeared have been conveniently summarised by Warburg himself in two publications [52] and since the whole field of investigation presents, apart from the intrinsic results obtained, certain interesting features of technique, it is judged appropriate to submit in the present Report a review of the problems encountered. The reader will find some reference to the earlier phases of these investigations in the Report by Professor J. C. Drummond for 1924.[53] Warburg has shown from a study of Flexner–Jobling rat carcinoma, Jensen rat sarcoma, and Rous hen sarcoma, as well as of tumours of human origin, that such cancerous growths resemble certain yeasts in being able to metabolise carbohydrates by oxidative (respiratory) and glycolytic (fermentative) processes. But whilst normal tissues under aerobic conditions make use almost exclusively of oxidative processes, they may under anaerobic conditions form lactic acid, thus exhibiting a glycolytic or fermentative function. Warburg has shown that a peculiarity of the cancer cell is its power, under aerobic conditions, of making use of both these processes in metabolising carbohydrates. Isolated tumour cells, even in the entire absence of oxygen and for so long as they are supplied with glucose, may flourish for some time, utilising carbohydrate anaerobically. Thus after 48 hours under the strictest anaerobiosis Rous sarcoma cells still flourished and could be transplanted aerobically. Normal tissue cells from which the cancerous growths are formed do not exhibit such capacity to exist by purely glycolytic processes. Thus under comparable conditions excised intestinal mucous membrane forms only about one-tenth of the amount of lactic acid formed by a carcinoma developed from the mucous membrane. On the other hand the metabolism of the cells of certain embryos in a very early stage of development shows a much greater affinity to that of the cancer cell than does the adult tissue cell.

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[52] "Über den heutigen Stand des Carcinomproblems," Berlin (Julius Springer), 1926, and "Über die katalytischen Wirkungen der lebendigen Substanz," Berlin (Julius Springer), 1928.

[53] *Ann. Reports*, 1924, **21**, 208.

For the study of such problems in tissue metabolism Warburg has elaborated a manometric technique to which the following considerations apply. Measurements are made of respiration, that is, oxygen consumption (1), aerobic glycolysis (2), and anaerobic glycolysis (3), and these are expressed in the form of quotients symbolised respectively as Q_{O_2} (1), $Q_{M}^{O_2}$ (2), and $Q_{M}^{N_2}$ (3), the value of the quotients being obtained by dividing the cubic millimetres of oxygen consumed (1), the cubic millimetres of carbon dioxide evolved as a result of lactic acid formation in the presence of oxygen (2), and the cubic millimetres of carbon dioxide evolved as a result of lactic acid formation in the presence of nitrogen (3), each by the dry weight in milligrams of the tissue used multiplied by the duration of the observation in hours. The Meyerhof quotient may then be calculated from :

$$\frac{\textit{Anaerobic glycolysis—Aerobic glycolysis}}{\textit{Respiration}},\ \textit{i.e.},\ \frac{Q_{M}^{N_2}-Q_{M}^{O_2}}{Q_{O_2}}$$

Assuming maximum efficiency of the Pasteur reaction, which correlates respiration with fermentation, the symbol U is used to indicate the excess fermentation, that is to say, the minimum theoretical value for the aerobic glycolysis, or, making use of the symbols already explained, $U = Q_{M}^{N_2} - 2Q_{O_2}$. When the Pasteur reaction is maximal, U (the calculated excess aerobic fermentation) is identical with that found, $Q_{M}^{O_2}$.[54] The main lines of Warburg's work suggest that the value U is positive for tumour tissue and negative for normal tissue, varying between −39 and zero. Exceptions are encountered in the case of the free-moving red and white cells of the blood, which show a positive U value, and of the retina cells, which show a greater glycolytic power than that of any other animal tissue and, like cancer tissue, give positive U figures. Furthermore, in the case of retina cells the value of $dQ_{M}^{N_2}/dt$ is positive, whereas it is negative for normal tissues and zero for tumour tissues. The following convenient summary of the general results has been given by Warburg and Kubowitz :[55]

	Normal tissues except retina.	Carcinomas and sarcomas.	Retina.
$Q_{M}^{N_2}$	$\overset{=}{<}50$	$\overset{=}{<}50>20$	$\overset{=}{<}200$
$dQ_{M}^{N_2}/dt$	<0	0	>0
U	$\overset{=}{<}0$	>0	>0

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[54] Warburg, *Biochem. Z.*, 1927, **184**, 484.

[55] *Ibid.*, 1927, **189**, 242.

An important extension of the observations which we have just discussed has been made by Crabtree[56] in a study of the carbohydrate metabolism of pathological overgrowths other than those of the malignant type so thoroughly investigated by Warburg and his collaborators. The growths studied by Crabtree were those of fowl-pox, vaccinia lesions in young chickens and in rabbits, and human warts. The fowl-pox lesions showed, in nearly every case investigated, a positive excess fermentation making them fall into the category of malignant tumours so far as their metabolism is concerned. Vaccinia lesions in young chickens and human warts also exhibited a metabolism corresponding in type to that of malignant tissue, the magnitude of the respiration and the aerobic and anaerobic glycolysis approximating to that found for tumours. In the case of vaccinia lesions in rabbits the slight increase in the metabolic activity observed is thought possibly to be due to the invasion of the tissue by leucocytes, which show, as already mentioned, a positive U value. The general conclusion arrived at by Crabtree is that the magnitude and relationships of the respiratory and glycolytic processes, found by Warburg to be characteristic of malignant tissues, are shared in common with the latter by pathological overgrowths generally. A further interesting observation was made by Crabtree in investigating the metabolism of Rous chicken sarcoma during development. The tumours were developed in the breast muscle, and during the first two days after the injection of the cell-free filtrate used as inoculum, a slight increase in the metabolic activity of the muscle was noted. This was possibly due to leucocytic invasion, since it was followed by a return to the normal low values of the undisturbed muscle. Only when a histological examination showed foci of tumour cells scattered through the muscle was any real increase found in the metabolism quotients. The figures obtained showed a rough correspondence in their magnitude to what might be theoretically calculated from the proportion of tumour tissue seen microscopically. It is concluded that the tumour cells possess their characteristically high metabolic rate from the time of their appearance rather than that a progressive development of this metabolism takes place over a transitional period. One must therefore infer that these peculiar metabolic phenomena are a result rather than the cause of pathological overgrowths.

The Chemistry of Internal Secretions.

Thyroxine.—The important work of Harington and Barger on the constitution and synthesis of thyroxine was fully dealt with in an earlier Report.[57] This year there falls to be recorded the resolution of *dl*-thyroxine by Harington.[58] β-[3 : 5-Di-iodo-4-(4′-hydroxyphenoxy)phenyl]-α-aminopropionic acid, to which the name 3 : 5-di-iodothyronine is given, was converted into its formyl derivative by warming with formic acid. Attempts to resolve the formyl derivative by means of alkaloid salts failed. Success was attained by the use of *l*-α-phenylethylamine and although the insoluble fraction of the resulting salt mixture could not be obtained optically pure, the soluble fraction, after two or three recrystallisations, showed no further change in rotation, the value being $[\alpha]_{5461}$ + 23·8°. On decomposition this salt yielded formyl-*l*-3 : 5-di-iodothyronine, $[\alpha]_{5461}$ + 27·8°, from which was obtained on hydrolysis with 15% hydrobromic acid *l*-3 : 5-di-iodothyronine, $[\alpha]_{5461}$ − 1·3°. The last-mentioned compound was then iodinated with iodine in ammoniacal solution to give *l*-thyroxine, $[\alpha]_{5461}$ −3·2°. A similar series of experiments carried out with *d*-α-phenylethylamine yielded in succession a soluble salt having $[\alpha]_{5461}$ − 21·9°, formyl-*d*-3 : 5-di-iodothyronine, $[\alpha]_{5461}$ − 26·9°, *d*-3 : 5-di-iodothyronine, $[\alpha]_{5461}$ + 1·15°, and finally *d*-thyroxine having $[\alpha]_{5461}$ + 2·97°. The possibility of racemisation during the final iodination process was excluded by an experiment in which *l*-tyrosine was iodinated, the resulting 3 : 5-di-iodotyrosine reduced to tyrosine, and the latter shown to possess its original rotation. In physiological tests *l*-thyroxine was found to possess some three times the activity of *d*-thyroxine. This new achievement is a noteworthy addition to Harington's previous brilliant work in this field.

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[56] *Biochem. J.*, 1928, **22**, 1289.

Insulin.—The work of Abel and his co-workers, of Funk, and of du Vigneaud on the crystallisation of insulin was dealt with in last year's Report.[59] The work described there has been continued by du Vigneaud and his collaborators.[60] Conditions for preparing crystalline insulin from the impure product have been standardised, and amongst the amino-acids isolated from the crystalline material after hydrolysis are cystine, tyrosine, arginine, histidine, leucine, and lysine. From a comparison of the total sulphur content of insulin with the amount of cystine present it is concluded that some sulphur compound other than cystine is present in the insulin molecule. A study of the nitrogen distribution in crystalline insulin has also been made.[61] Du Vigneaud, Geiling, and Eddy [62] bring forward evidence which considerably strengthens the view that the crystalline material is homogeneous. For instance, when crystalline insulin is adsorbed from $N/100$-hydrochloric acid by charcoal, and subsequently eluted with phenol, no change in activity is noted. Nor does the adsorbed material exhibit any differential solubility in disodium hydrogen phosphate solution. Moreover, the charcoal–phenol powder has been reconverted into crystalline insulin. When crystalline insulin is heated with $N/10$-hydrochloric acid at 100° for one hour, a precipitate forms which is insoluble in dilute acid and in disodium hydrogen phosphate solution. It dissolves in alkali and from the resulting solution there is obtained on acidification a product having the original solubility in acid and showing but slight loss of activity.

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[57] *Ann. Reports*, 1926, **23**, 234.

[58] Report of the Meeting of the Biochemical Society (Dec. 14th), *J. Soc. Chem. Ind.*, 1928, **47**, 1346.

[59] *Ann. Reports*, 1927, **24**, 261.

[60] *J. Pharm. Exp. Ther.*, 1928, **32**, 367, 387; **A.**, 553.

[61] Wintersteiner, du Vigneaud, and Jensen, *ibid.*, p. 397; **A.**, 553.

[62] *Ibid.*, 1928, **33**, 497; **A.**, 1160.

Jensen and Geiling [63] have succeeded in acetylating insulin by treating it with acetic anhydride at 0° for 15 hours. The product shows some 4·5% of acetyl groups. It is hydrolysed very rapidly by $N/100$-alkali at 0° and insulin is regenerated. The activity figures of these preparations are of great interest. They were as follows: for the original crystalline insulin, 45 units/mg.; for acetylinsulin, 8 units/mg.; and for the material regenerated by alkali treatment, 25 units/mg. Freudenberg and Dirscherl [64] have obtained results of a somewhat similar nature. Insulin precipitated from methyl alcohol by benzene was treated in pyridine at 0° with acetic anhydride for 3 hours and the resulting acetyl product, which was almost inactive, contained 3—4% of the acetyl group. Treatment with $0{\cdot}03N$-alkali at 1—3° for 24 hours gave a regenerated product with one-third to one-fifth of the activity of insulin. The regenerated product still contained 0·8% of acetyl groups. It is inferred that if insulin is a single substance acetylation probably affects hydroxy-, amino-, and imino-groups and of the resulting combinations only the acetoxy-groups are hydrolysed by dilute alkali. The main point of difference between the results of Freudenberg and Dirscherl and those of Jensen and Geiling lies in the much lower activity of the product regenerated by the former workers as compared with that of the latter workers. Jensen and Geiling [65] find that the lowered activity of the regenerated insulin is probably due to the loss of hydrogen sulphide, since even dilute sodium hydroxide solution eliminates some sulphur from acetylinsulin, whereas the original insulin is unaffected by treatment with the same concentration of alkali for 15 hours at 0°. It is suggested, therefore, that the lower activity of Freudenberg and Dirscherl's regenerated insulin is most probably due to the greater amount of decomposition which occurs with the more concentrated alkali used by them.

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[63] *J. Pharm. Exp. Ther.*, 1928, **33**, 511; **A.**, 1160.

[64] *Z. physiol. Chem.*, 1928, **175**, 1; **A.**, 675.

[65] *Loc. cit.*

The Liver Constituent curative of Pernicious Anæmia.—During the past two years an important advance in medicine has been achieved on the basis of the demonstration by Minot and Murphy [66] that in cases of pernicious anæmia the feeding of large amounts of liver is followed by an increase in the red blood cell count. From this observation there has been built up one of the most remarkably successful curative treatments credited to modern medicine. The curative effect is produced by some substance or substances present in normal mammalian liver and presumably lacking in the systems of sufferers from pernicious anæmia. The nature of the curative agent is at present unknown and the Reporter, in including a reference to this advance in the present section of this Report, does not wish to commit himself to the view that it is of the nature of an internal secretory product. None the less, its properties are suggestive of this, and in any case the term internal secretion is sufficiently wide to support the argument from convenience for including the reference here. Methods of investigating the potency of the various chemical fractions obtained from liver are based necessarily on feeding experiments carried out on cases of pernicious anæmia in the human subject, since it has not yet been demonstrated that the typical clinical picture of the disease is manifested in experimental animals. So successful has the cure proved that the Reporter is given to understand that a lack of patients is seriously hampering further investigations into the nature of the curative agent, surely a remarkable and unforeseen contingency !

Cohn, Minot, Alles, and Salter [67] have published an account of the preparation and properties of the active material obtained from liver. The latter was minced and brought to p_H 5·0 by the addition of sulphuric acid and the subsequent extraction ensured efficient removal of the water-soluble substances in which the active material is found. Coagulable protein was removed and the extract was concentrated under reduced pressure. The addition of alcohol to the resulting solution to produce a concentration of 70% gave a precipitate which was rejected, and the filtrate was again concentrated and poured into sufficient alcohol to produce a concentration of 95%. The aqueous solution of the resulting precipitate was cleared with basic lead acetate and, after removal of excess of lead, treated with phosphotungstic acid. The solution of the material obtained from the phosphotungstate precipitate was rich in the active substance. From the above method of concentration some idea will be gained of its nature. It is soluble in water and insoluble in ether and alcohol. Active preparations have been obtained free from proteins, carbohydrates, lipoids, and iron, and of the best of these preparations doses of 0·6 gram per day (calculated as ash-free organic matter) exercised a definite physiological effect. The active material contained, on an ash-free basis, about 19% of nitrogen. It seems to the Reporter that its properties, so far as they are known, are not incompatible with those of a salt of a fairly complex organic acid.

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[66] *J. Amer. Med. Assoc.*, 1926, **87**, 470; 1927, **89**, 759.

[67] *J. Biol. Chem.*, 1928, **77**, 325; **A.**, 790.

Unsaponifiable Constituents of Animal Oils and Fats.

In recent years considerable attention has been given to the nature of the constituents of fish liver oils. The stimulus to such studies has been in part the chemical investigation of the unsaponifiable fraction of oils and fats containing vitamins-*A* and -*D*, but the field has intrinsic attractions of its own and provides a remarkably interesting chapter in animal biochemistry. In this field much of the earlier work, which stands to the credit of Japanese investigators, notably Tsujimota and Toyama, has been conveniently reviewed by Heilbron.[68]

Prominent amongst the constituents of the unsaponifiable fraction of most elasmobranch fish liver oils are three alcohols, batyl, selachyl, and chimyl. With these are found a hydrocarbon, squalene, which alone sometimes comprises some 80% of the oil, and cholesterol. The two first-mentioned alcohols are the subject of a recent communication by Heilbron and Owens.[69] They assign to batyl alcohol the formula $C_{21}H_{44}O_3$, which is one of the alternatives first suggested by the Japanese investigators already mentioned. It is a saturated dihydric alcohol and the main question concerning its constitution has centred round the nature of the third oxygen atom. Weidemann [70] was of the opinion that this was present as a methoxyl group, but Heilbron and Owens now show that the action of hydriodic acid on the alcohol is to liberate octadecyl iodide, and they conclude that the parent alcohol is a monoglyceryl ether of octadecyl alcohol having the constitution $C_{18}H_{37}\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ or $C_{18}H_{37}\cdot O\cdot CH(CH_2\cdot OH)_2$. From the known analogies between this alcohol and selachyl and chimyl alcohols, the former, which has the formula $C_{21}H_{42}O_3$ and is the olefinic analogue of batyl alcohol, must be the monoglyceryl oleyl ether, and chimyl alcohol, $C_{19}H_{40}O_3$, the monoglyceryl cetyl ether. The occurrence of such glyceryl ethers in nature, forming a link between the fats and waxes, is a matter of great biological interest, the inter-relationships of the three types of compound being expressed as follows :

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[68] Report of the Food Investigation Board, 1927, Section G.

[69] *J.*, 1928, 942; **A.**, 616. · [70] *Biochem. J.*, 1926, **20**, 685; **A.**, 1926, 980.

Fat	$(R\cdot CO\cdot O)_3C_3H_5$
Wax	$R\cdot CO\cdot OR'$
Ethers	$R'O\cdot C_3H_5(OH)_2$

Squalene, the hydrocarbon already mentioned, is an open-chain dihydrotriterpene with the formula $C_{30}H_{50}$ and the question of its constitution was dealt with in the Report of last year.[71] From the nature of the products isolated from the oxidation by means of ozone of squalene and of an incompletely hydrogenated squalene corresponding to a decahydrosqualene, Heilbron[72] now considers the main problem of the constitution of this hydrocarbon to be elucidated. Its formation can be visualised as the " head to tail " linking of six isoprene nuclei and it is probably synthesised in the living organism by aldol condensations of aliphatic plant terpene aldehydes such as citral ($C_{10}H_{16}O$), citronellal ($C_{10}H_{18}O$), or farnesal ($C_{15}H_{24}O$), followed by reduction in the animal liver.

Interesting data concerning the unsaponifiable matter from the stomach oil of an elasmobranch fish, *Scymnorhinus lichia*, have been reported by Kamm.[73] The unsaponifiable matter from this oil proved to consist mainly of squalene (98%) associated with 0·28% of batyl alcohol and 0·96% of a residue consisting chiefly of selachyl alcohol. The oil, of which the function in the stomach is unknown, is therefore similar in nature to the liver oil of elasmobranchs generally. The problem of the biological significance of these unsaponifiable constituents of oils is being studied by Channon. In the case of fish oils,[74] it is found that the elasmobranch liver oils differ from those of the teleosts in containing much larger amounts of unsaponifiable matter, and in the elasmobranch oils the higher the percentage of unsaponifiable matter in a given oil the lower is the sterol content of that fraction. This low percentage of sterol is not due to the presence of squalene as such but to the quantity in which it is present, for the relationship between sterol and the unsaponifiable fraction is maintained throughout whether squalene is present or not. No evidence is therefore obtained of any relationship between sterol and squalene. None the less the question of the origin of this curious hydrocarbon is an interesting one. Channon adduces evidence which suggests that it must be synthesised by the animal and not derived from its foodstuff—a view which is in agreement with Heilbron's speculations already referred to.

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[71] *Ann. Reports*, 1927, **24**, 127.

[72] *Loc. cit.*

[73] *Biochem. J.*, 1928, **22**, 77; **A.**, 319.

[74] *Ibid.*, p. 51; **A.**, 319.

The Vitamins.

Vitamin-A.—Following on the subject matter dealt with in the preceding section of this Report it is judged advisable to give some account of recent chemical studies of the vitamin-*A* fraction of certain liver oils carried out by Drummond and Baker.[75] That portion of the unsaponifiable fraction of cod-liver oil in which vitamin-*A* is found is known to consist of unsaturated alcohols of high molecular weight. Efforts to prepare from it crystalline phthalates or substituted phthalates were not successful, nor could any satisfactory fractionation be obtained on distilling the cholesterol-free material at very low pressures. Considerable loss of the vitamin occurred. The unsaturated substances present in the vitamin fraction proved to be resistant to hydrogenation, thus supporting the view that they have a complex ring structure of the type of the unsaturated sterols and higher terpenes. Comparative studies were then instituted between the unsaponifiable fractions of liver oils from different animals and possessing different vitamin-*A* contents. Those selected were cod-liver oil, sheep-liver fat, Japanese and Greenland shark-liver oils having the relative vitamin activities 13 : 21 : 6 : 1. The fraction from sheep-liver fat contains, in addition to cholesterol, a relatively large quantity of an unsaturated hydrocarbon which is not squalene but which resembles that described by Channon and Marrian.[76] Attempts to distil the unsaponifiable material from sheep-liver fat proved to be a complete failure: the hydrocarbon decomposed and only about 15% of the vitamin was recovered. Better results were obtained from the shark-liver oils. In the case of the Greenland shark oil, which contained less vitamin-*A* than the Japanese oil, the more solid fraction was almost devoid of vitamin-*A* and consisted of a mixture of cholesterol and chimyl alcohol. The liquid fraction gave a good distillation curve indicating that it consisted largely of one or two substances. Hydrogenation of this fraction gave large amounts of octadecyl and batyl alcohols, which were formed respectively from the oleyl and selachyl alcohols of the original distilled material. Squalene was also present but only in traces. The Japanese oil, although much richer than the Greenland oil in vitamin-*A*, gave an unsaponifiable fraction of similar composition. Chimyl alcohol and cholesterol were obtained and by hydrogenating the distillation products of the sterol-free material an almost quantitative yield of batyl alcohol was obtained. Some 40% of the vitamin survived the distillation of this material. From these results it is estimated that of the unsaponifiable matter of these two shark-liver oils at least 95% has been separated in the form of identifiable substances which are not believed to be related either directly or indirectly to vitamin-*A*. The evidence suggests that the latter, like vitamin-*D*, is a sterol derivative present in liver oils in extremely low concentrations, and Drummond and Baker come to the disappointing but inevitable conclusion that the direct chemical attack on vitamin-*A* is virtually useless.

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[75] Report of the Meeting of the Biochemical Society (Dec. 14th), *J. Soc. Chem. Ind.*, 1928, **47**, 1346.

[76] *Biochem. J.*, 1926, **20**, 409; **A.**, 1926, 638.

Improvements in the methods available for the detection and assay of vitamin-*A* have received considerable attention. Hume and Smith [77] have studied the evaluation of vitamin-*A* by means of growth curves of rats. The technique used involved a depletion period during which *D* was supplied by ultra-violet irradiation. Graded amounts of *A* were then administered in the form of spinach, daily doses of from 0·2 to 1·0 gram being given, and the conclusions arrived at are as follows: (*a*) With no dose or a very small dose there is no recovery. (*b*) With small doses there is sub-normal growth graded quantitatively to the dose and followed by a premature slackening. (*c*) With larger doses there is normal growth for a time, followed by premature slackening. (*d*) With an optimal dose there is normal growth to maturity. It is suggested that the evaluation of *A* is best made by dispensing with the depletion period, or if it is used, by employing only doses which are likely to give the responses (*a*) and (*b*). With regard to the foregoing suggestions Coward and Key [78] point out that such responses as those obtained by Hume and Smith have also been observed by them, but on the other hand certain substances containing vitamin-*A* give sub-normal growth graded to the dose but not followed by any premature slackening. Thus the rate of growth has been observed to remain unaltered and sub-normal for unusually long periods, some of the rats used attaining maturity only after about 40 weeks on the experimental diet. The importance of a long test of eight or more weeks is emphasised. Sherman and Burtis [79] point out that the greater the weight of the test animal the less is its gain in weight with a given intake of vitamin-*A* and it is considered best to adhere to an eight-week period for the test and to a standard weekly gain in weight of 3 grams. Shortening of the test period tends to give variable and higher results for the vitamin-*A* content of the material under test, and a higher standard rate of gain of weight decreases the delicacy of the method without increasing its accuracy.

The specific arsenic and antimony trichloride colour tests for

[77] *Biochem. J.*, 1928, **22**, 504; **A.**, 555. [78] *Ibid.*, p. 1019; **A.**, 1058.

[79] *J. Biol. Chem.*, 1928, **78**, 671; **A.**, 1161.

vitamin-*A* have also received considerable attention during the past year. Steudel and Peiser [80] cast some doubt on the specificity of the antimony chloride reaction and state that a whale oil examined by them gave the colour reaction when diluted in chloroform in concentrations of 2 and 0·2%, whereas similar dilutions of the oil in a vitamin-free hardened vegetable oil failed to relieve the condition of rats kept on a diet lacking in *A*. These conclusions are diametrically opposed to those of earlier workers and therefore merit further attention, bearing in mind the fact that, although many cases of parallelism between the intensity of the colour reaction and the vitamin-*A* potency have been observed, rigid proof of a direct relationship between the two is still lacking. The evidence is admittedly strong but circumstantial. Wokes [81] has made a careful investigation of the fairly permanent colours given by the usual reagents with sterols and their derivatives, and compared them with the transient colours ascribed to vitamin-*A*. The latter have also been investigated spectroscopically. It is found that irradiation of the sterols tends to make the colours more transient and on the other hand a physiologically tested cod-liver oil was found to give with antimony chloride a " vitamin " blue which it was found possible to make persist for nearly an hour. One characteristic property of the " vitamin " colour is the sequence of the change from blue to red. With the sterols the characteristic change is red ⟶ blue and possibly red again. It has, however, been possible to get a blue ⟶ red reaction from cholesterol irradiated at its melting point or oxidised under given conditions with certain reagents including benzoyl peroxide. A somewhat similar observation has been made by Rosenheim,[82] but the chromogen so produced was shown to differ from the " vitamin " chromogen. In his spectroscopic investigations Wokes has shown that the colour obtained with oils containing vitamin-*A*, when tested with arsenic chloride, shows bands at about 587 and 475 $\mu\mu$ and with antimony trichloride at about 614 and 530 $\mu\mu$. In each case the maximum absorption shifts from the band of longer wave-length to the shorter one when the chromogen is left in contact with the reagents, the change corresponding to the blue ⟶ red transition.

The possibility of developing still another method for detecting vitamin-*A* is suggested by the observations of Morton and Heilbron,[83] who conclude from a spectroscopic examination of various oils and other preparations that the presence of the vitamin is characterised by an absorption band in the ultra-violet with a maximum at 328 $\mu\mu$. It is also suggested that one of the decomposition products of the vitamin has an absorption band near 275 to 285 $\mu\mu$.

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[80] *Z. physiol. Chem.*, 1928, **174**, 191; **A.**, 925.

[81] *Biochem. J.*, 1928, **22**, 830, 997; **A.**, 800, 1058.

[82] *Ann. Reports*, 1927, **24**, 243. [83] *Biochem. J.*, 1928, **22**, 987; **A.**, 1058.

An extremely interesting observation regarding the formation of vitamin-*A* has been made by Moore,[84] who finds that etiolated wheat shoots, fed to rats under conditions involving the minimum of red light illumination consistent with the feeding and handling of the animals, are an efficient source of vitamin-*A*. It is concluded that light is not essential during any stage of the formation of the vitamin from the seed, or alternatively, if light is required, extremely short exposures to dim red light are effective.

Variations in the stability of vitamin-*A* from various plant sources are described by Sherman, Quinn, Day, and Miller.[85] For instance, when tomato juice was heated at 97° in an atmosphere of nitrogen for four hours, 17% of the vitamin was destroyed and this rate was not affected by changing the p_H of the juice from its natural value of 4·2 to 9·2. Similar treatment in olive oil solution of the vitamin extract from dry spinach and from butter fat resulted in a destruction of 20% and 33% respectively. Steudel[86] had previously reported that the vitamin-*A* of brain tissue is very sensitive to heat except when dissolved with its lipoid complement in fat or other suitable medium.

The B *Vitamins.*—The multiple nature of what was formerly called vitamin-*B* was dealt with in the Report of last year[87] and much work published since goes to corroborate and extend this discovery. The evidence in favour of the dual nature of this vitamin complex is strengthened by fresh data brought forward by Kennedy and Palmer,[88] Salmon, Guerrant, and Hays,[89] Evans and Burr,[90] Chick and Roscoe,[91] Hunt,[92] Hogan and Hunter,[93] Hunt and Krauss,[94] and by Levene.[95] Indeed a more complex tripartite nature is suggested in the investigations of Williams and Waterman[96] and of Hunt.[97] One of the most interesting results obtained from a chemical point of view is that of Levene,[98] who has shown that by deaminising with nitrous acid an Osborne and Wakeman yeast concentrate, and subsequently treating it with a silica gel, the adsorbate contains only the heat-labile vitamin-B_1. Daily doses of 0·07 mg. of this material were sufficient to maintain the normal growth of white rats. One must assume that vitamin-B_2 is inactivated through loss of amino-groups. Kinnersley and Peters,[99] in continuing their studies on vitamin-B_1 of yeast, have succeeded in obtaining concentrated preparations curative of polyneuritis in pigeons in daily doses of 0·027 mg. They find that the solubility of the vitamin in alcohol varies with the activity of the preparation and with the p_H of the solution treated with the alcohol. It is not soluble in chloroform, carbon tetrachloride, ether, acetone, or ethyl acetate. This observation corrects certain erroneous statements which have gained some currency in the literature. There are certain suggestions in the work described by Kinnersley and Peters that in the aqueous extract of yeast vitamin-B_1 may occur in two forms.

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[84] *Biochem. J.*, 1928, **22**, 1097; **A.**, 1058.

[85] *J. Biol. Chem.*, 1928, **78**, 293; **A.**, 1058.

[86] *Z. physiol. Chem.*, 1927, **170**, 13; **A.**, 1928, 92.

[87] *Ann. Reports*, 1927, **24**, 244.

[88] *J. Biol. Chem.*, 1928, **76**, 591; **A.**, 555.

[89] *Ibid.*, p. 487; **A.**, 556.

[90] *Ibid.*, 1928, **77**, 231; **A.**, 676.

[91] *Biochem. J.*, 1928, **22**, 790; **A.**, 800.

[92] *J. Biol. Chem.*, 1928, **78**, 83; **A.**, 926.

[93] *Ibid.*, p. 433; **A.**, 1059.

[94] *Ibid.*, 1928, **79**, 733; **A.**, 1405.

[95] *Ibid.*, p. 465; **A.**, 1405.

[96] *Ibid.*, 1928, **78**, 311; **A.**, 1058.

[97] *Ibid.*, 1928, **79**, 723; **A.**, 1405.

[98] *Loc. cit.*

In regard to the question of the possible tripartite nature of "vitamin-B" two independent but very similar investigations by Williams and Waterman [1] and by Hunt [2] are of interest. In the first-mentioned paper it is shown that pigeons kept on a synthetic diet in which adequate supplies of purified B_1 and B_2 fractions were present, showed a marked improvement when air-dried brewer's yeast was added to the diet. B_1 was supplied as a fuller's earth adsorbate of a dialysed yeast extract, and B_2 as autoclaved yeast. In the second investigation the two fractions were also separated by means of fuller's earth and, although they were found to supplement each other in maintaining the growth of rats, they failed to produce so good an effect as an equivalent amount of fresh yeast. In both instances the presence of a third accessory food constituent in yeast is deduced in order to explain these results.

Vitamin-C.—In last year's Report [3] attention was directed to the interesting discovery by Zilva that the antiscorbutic activity of decitrated lemon juice is associated with a capacity for reducing phenolindophenol to its leuco-base, and in a further communication [4] the investigation of this relationship is continued. When phenolindophenol is added to decitrated lemon juice until the indicator is no longer reduced, and the solution is adjusted immediately to p_H 7, the antiscorbutic activity disappears within 24 hours. Purified antiscorbutic fractions from lemon juice lose their activity much more rapidly than does decitrated lemon juice of similar activity. Decitrated lemon juice, dialysed in collodion thimbles of a permeability which leaves the solution inactive after 3 days, loses the capacity for reducing phenolindophenol. This reducing capacity is retained to a great extent by the juice when dialysed in thimbles of a permeability which yields an active juice at the end of the dialysis. Acidity retards deterioration on storage of the antiscorbutic activity in anaerobically autoclaved decitrated lemon juice.

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[99] *Biochem. J.*, 1928, **22**, 419; **A.**, 556.
[1] *Loc. cit.*
[2] *Loc. cit.*
[3] *Ann. Reports*, 1927, **24**, 247.
[4] *Biochem. J.*, 1928, **22**, 779; **A.**, 801.

On storage at p_H 3, however, the deteriorating effect of autoclaving is scarcely perceptible. Lemon juice autoclaved anaerobically, even in a very acid medium, deteriorates much more rapidly at p_H 7 on storage than similar solutions which have not been autoclaved. Comparatively little loss occurs in decitrated lemon juice which has been autoclaved at 40 lb. pressure for 1 hour under strictly anaerobic conditions. These results would seem to justify Zilva's earlier suggestion that the stability of the antiscorbutic vitamin in lemon juice is conditioned by the presence of a reducing principle and of another constituent, the functioning of which is destroyed by heat.

*Vitamin-*D *and Ergosterol.*—Much important work falls to be reviewed in this section of the Report. Dealing first with the question of the specificity of ergosterol as the substance from which vitamin-*D* is formed by irradiation, attention is directed to a careful resumé of the position by Rosenheim and Webster.[5] The characteristic general features of the sterol structure are the presence in the molecule of a hydroxyl group, of one or more unsaturated linkages, and of a system of four reduced rings. The question of the part played by the hydroxyl group in the activation process is difficult to decide. Rosenheim and Webster [6] had already shown that two esters of ergosterol, the acetate and the benzoate, are rendered by irradiation as highly antirachitic as the sterol itself, and more recently von Euler, von Euler, and Rydbom [7] have made a similar observation with regard to diergosteryl phosphate, which when irradiated is powerfully antirachitic and promotes growth in rats in doses of 0·0002 mg. per day. Such activation may, however, be preceded by a photochemical hydrolysis and, as Rosenheim and Webster point out, it is not yet possible to determine experimentally the bearing of the hydroxyl group on the question of activation. On the other hand, it is clear that not only the presence but the number of double bonds is a deciding factor in the photochemical production of vitamin-*D*. The naturally occurring saturated sterols coprosterol and α-amyrol and the artificially reduced sterols dihydrocholesterol and dihydrositosterol all remain inactive after irradiation. Moreover, neither cholesterol nor sitosterol with one double bond, nor stigmasterol, cholesterylene, oxycholesterylene, and dihydroergosterol (Windaus and Brunken [8]) with two double bonds can be activated. The slight activity noted by Hess and Anderson [9] in irradiated sitosterol is without doubt due to slight admixture with ergosterol, and a similar explanation accounts for the activity observed by Jendrassik and Keményffi [10] in cholesterol

[5] *Nature*, 1928, **121**, 570; **A.**, 557; *Biochem. J.*, 1928, **22**, 762; **A.**, 801.
[6] *Lancet*, 1927, ii, 622.
[7] *Biochem. Z.*, 1928, **199**, 276; **A.**, 1406.
[8] *Annalen*, 1928, **460**, 225; **A.**, 424.
[9] *Ann. Reports*, 1927, **24**, 250.
[10] *Ibid.*, p. 249.

irradiated after bromine purification, since Bills, Honeywell, and MacNair[11] find that ergosterol is not entirely removed from cholesterol by bromination or by treatment with charcoal, some 3% still remaining. There can therefore be little doubt that of the compounds mentioned above ergosterol and its esters alone give rise on irradiation to the vitamin. Rosenheim and Webster have also shown that *iso*ergosterol, which is obtained from ergosterol hydrochloride by the removal of hydrogen chloride, cannot be activated, and another isomeride, *neo*ergosterol, likewise remains inactive (Windaus and Borgeaud[12]). Very recently Rosenheim and Webster[13] have shown that fungisterol, which accompanies ergosterol in ergot, and two other sterols from the same source remain biologically inactive after irradiation, and Hume, Smith, and Smedley-MacLean[14] have made a similar observation regarding a zymosterol (from yeast). Oxidation equally with reduction destroys the capacity of ergosterol to form the vitamin, since Windaus and Brunken[15] have demonstrated the inactivity of irradiated ergosterol peroxide. On the other hand, ergosterol regenerated from the peroxide can be activated. It is of interest to note in passing that the peroxide is prepared from ergosterol by photo-oxidation in 95% alcohol solution in the presence of eosin and under the influence of the visible radiations of a powerful filament lamp. From the foregoing results and others, which need not be detailed here, one has every confidence in concluding that ergosterol alone of all the numerous pure substances examined possesses the property of forming vitamin-*D* under the influence of ultra-violet light.

Much important work has appeared during the past year on the ultra-violet absorption spectrum of ergosterol and its irradiated products. A careful investigation of this question has been made by Webster and Bourdillon.[16] They find that ergosterol examined after short periods of irradiation shows an increase in absorption, which is at a maximum after a period depending on the concentration of the solution and the intensity of radiation. On further irradiation the absorption decreases steadily to almost complete disappearance. The antirachitic effect and the absorption are produced at approximately the same rate. On further irradiation of the active products, after the removal of ergosterol, the antirachitic activity and the absorption decrease and eventually disappear after irradiation for three to five hours. It is deduced that the irradiation of ergosterol probably produces two substances in succession, one with a maximum absorption at 280 or 290 μμ, which is probably the vitamin, and a second with a maximum at about 230 μμ. In relation to this question an interesting hypothesis has been suggested by van Wijk and Reerink.[17] It is that ergosterol has two systems of absorption bands connected with different parts of the molecule. By irradiation such that vitamin-*D* is formed the first system with maxima at 293, 281, and 270 μμ (see also Heilbron, Kamm, and Morton [18]) makes way for the characteristic absorption band of *iso*ergosterol at a little below 250 μμ, which would mean that the corresponding part of the molecule undergoes the same change in constitution by irradiation as by the transformation of ergosterol into *iso*ergosterol by the chemical method of Reindel, Walter, and Rauch.[19] Another part of the molecule obviously does not change its constitution, which is deduced from the permanence of the second system of bands at 262 and 250 μμ. Like vitamin-*D*, *iso*ergosterol remains unchanged by irradiation with ultra-violet light of wave-length longer than 270 μμ and is destroyed by light of wave-length of about 250 μμ, as is shown by the disappearance of the absorption bands. Recently published results of Bills, Honeywell, and Cox [20] substantially corroborate these suggestions in that it is shown that the photochemical product which shows an absorption maximum at 248 μμ is not vitamin-*D*, for the appearance of this band coincides, not with the development, but with the destruction of antirachitic potency. The last-mentioned workers further suggest that, although oxidation processes play no part in the formation of vitamin-*D*, they appear to be at least one cause of the destruction of the substance with a band at 248 μμ. The latter is supposed to be a substance having a molecular configuration similar to that of *iso*ergosterol. Van Stolk, Dureuil, and Heudebert [21] find that an alcoholic solution of pure ergosterol shows absorption maxima at 293·2, 281·5, 270·0, and 260·0 μμ. Irradiation by the light of a mercury vapour lamp from which all radiations shorter than 255·0 μμ have been screened produces a very slow formation of the vitamin. Irradiation by the total light of a hydrogen lamp in an atmosphere of nitrogen results in the disappearance of the first three bands, an increase in the intensity of the fourth, and the appearance of bands at 250·3 and 240·5 μμ. At the same time vitamin-*D* is formed in quantity.

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[11] *J. Biol. Chem.*, 1928, **76**, 251; **A.**, 332.

[12] *Annalen*, 1928, **460**, 235; **A.**, 425.

[13] Report of the Meeting of the Biochemical Society (Dec. 14th), *J. Soc. Chem. Ind.*, 1928, **47**, 1348.

[14] *Biochem. J.*, 1928, **22**, 980; **A.**, 1059.

[15] *Loc. cit.*

[16] *Ibid.*, p. 1223; **A.**, 1228.

Bills and Brickwedde [22] have stated that cholesterol (impure) can be activated by ultra-violet light at a temperature of −183°, and a more detailed account of similar experiments on ergosterol has been given by Webster and Bourdillon,[23] who have investigated the effects of temperatures ranging from +77·8° to −195° on the rate of activation of the sterol. The observed lack of marked effect of changes of temperature between +78° and −18° on the reaction of activation shows that the temperature coefficients of the changes causing production and destruction of the vitamin are not widely different, and the very moderate effect of lowering the temperature to −180° suggests that the temperature coefficient of both reactions is very small and hence that both reactions are directly photochemical in nature.

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[17] *Nature*, 1928, **122**, 648.

[18] *Biochem. J.*, 1927, **21**, 1279; **A.**, 1928, 92.

[19] *Annalen*, 1927, **452**, 34; **A.**, 1927, 241.

[20] *J. Biol. Chem.*, 1928, **80**, 557.

[21] *Compt. rend.*, 1928, **187**, 854; **A.**, 1406.

[22] *Nature*, 1928, **121**, 452; **A.**, 557.

Interesting speculations have been published by Fosbinder, Daniels, and Steenbock,[24] Kon, Daniels, and Steenbock,[25] and Coward [26] regarding the minimum dose of vitamin-*D* which is capable of being detected physiologically. In the first-mentioned investigation the energy absorbed by cholesterol during activation by means of monochromatic light of wave-length 265 $\mu\mu$ is measured with accuracy. It is found that the minimum time of irradiation required to produce a positive effect in the "line" calcification test is 22·5 seconds, during which time the energy absorbed is 234 ergs. The number of quanta absorbed is calculated as $3{\cdot}2 \times 10^{13}$. Applying Einstein's law of photochemistry, this would imply that $3{\cdot}2 \times 10^{13}$ molecules of vitamin-*D* had been synthesised and, assuming the molecular weight of the vitamin to be approximately the same as that of the sterol, from the number of gram-molecules produced (5×10^{-11}), the weight of vitamin-*D* generated in this experiment was calculated as $5 \times 10^{-11} \times 385 = 2 \times 10^{-8}$ gram. This was not a daily dose but the whole dose required during the test period of ten days. In the second investigation mentioned above, similar considerations are applied to ergosterol and from this basis the minimum detectable amount of the vitamin is estimated as 6×10^{-8} gram. Using a standard solution of irradiated ergosterol, Miss Coward finds that 2×10^{-5} mg. is the minimal daily dose producing a positive result in Steenbock's methods of assay. This corresponds to a consumption of 2×10^{-7} gram in 10 days. Assuming that rather less than 10% of the irradiated ergosterol is vitamin-*D*, a conclusion based on the results of Rosenheim and Webster,[27] the amount of the vitamin present in the latter quantity would be 2×10^{-8} gram. These various results seem to be remarkably concordant and one has every confidence that they give a fairly accurate measure of the potency of vitamin-*D*.

A. C. CHIBNALL.
JOHN PRYDE.

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[23] *Loc. cit.*

[24] *J. Amer. Chem. Soc.*, 1928, **50**, 923; **A.**, 557.

[25] *Ibid.*, p. 2573; **A.**, 1288.

[26] *Biochem. J.*, 1928, **22**, 1221; **A.**, 1288.

[27] *Loc. cit.*

CRYSTALLOGRAPHY

"An Introduction to Crystal Analysis," by Sir William Bragg,[1] is founded on a course of lectures at the University College, Aberystwyth, given in 1926. It is primarily intended for readers whose main interests lie in other branches of science, but who wish to understand the principles of analysis and its possible applications. The book will be welcome as a non-technical and readable account of all branches of the subject. "Strukturbestimmung mit Röntgeninterferenzen" by H. Ott [2] adds to the increasing list of books on X-ray analysis. All working in this branch of science will find the book of interest for its thorough treatment and inclusion of the most recent results.

"Materialprüfung mit Röntgenstrahlen" by R. Glocker is devoted to the technique of all methods of studying materials with X-rays. It contains an interesting section dealing with the determination of crystal structure, size, orientation, and deformation, and with crystal chemistry, and the structure of alloys. It is of importance to those concerned with the technical application of X-ray analysis.

Crystal Physics.

One of the most interesting, and, at the same time, one of the most difficult tasks of crystallography is to link up the known physical properties of real crystals with their structures as determined from X-ray measurements. The quantitative agreement between the calculated and the observed values of most of the physical constants of crystals is, at the present time, very poor. This is no doubt due largely to the fact that the mathematician deals in his calculations with an ideally regular crystal lattice, whereas these do not as a rule occur in nature, even in the so-called single crystals. The imperfections of the lattice are of two main kinds—large-scale imperfections, due to the fact that almost all crystals consist of a number of smaller fragments whose orientations, although nearly the same, differ slightly; and small-scale imperfections due to irregularities, probably extending over only a few atoms, in the lattice itself. These minute irregularities have been studied by A. Smekal,[3] who identifies them with the centres of the phosphoresence which many real crystals show. Certain crystals, notably the alkali halides, become coloured when exposed to light of suitable wave-length. Smekal points out that, in such minute "scars" in an ionic lattice, electrons will be released from the anions, by the action of light, more easily than in the lattice as a whole. He attributes the coloration to the release of an electron from an anion, and its subsequent combination with a neighbouring kation to form a coloured neutral ion. The irregularities are uniformly distributed, and about one atom in 10,000 appears to be affected in the average crystal. A crystal under mechanical stress will yield at such points of weakness first of all, and once yielding has begun, it will be followed by a breakdown of the structure. The mechanical strength of the crystal will thus be much less than would have been expected from the lattice structure alone.

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[1] G. Bell & Sons.

[2] "Handbuch der Experimentalphysik," Bd. 7, Akad. Verlagsges., Leipzig.

The question of crystal perfection and its relation to physical properties was also dealt with by C. H. Desch [4] in a paper introductory to a discussion on Cohesion and Related Problems, held by the Faraday Society in November 1927. J. E. Lennard-Jones and (Miss) B. M. Dent,[5] in the course of the same discussion, read a paper on Cohesion at a Crystal Surface. They considered the attractive force on a charged ion near a (100) face of an ionic crystal of the rock-salt type. This force can be considered as made up of four parts: (1) the direct electrostatic attraction of the charge on the ion by the valency charges of the ions of the crystal, (2) the attraction between these ions and the dipole produced by the polarisation of the attracted ion by the field near the surface, (3) the force due to the polarisation of the surface ions by the attracted ion, and (4) the force of attraction known to exist between neutral atoms, which is conveniently termed the van der Waals attraction. It is shown that, although at very small distances from the surface the electrostatic forces are much greater than the van der Waals attraction, at greater distances the latter predominates, so that it acts as the first agent in the adsorption of atoms or ions at a crystal surface, the electrostatic forces serving to complete the final capture.

Intimately connected with this subject is the question of crystal growth, which has been studied recently by W. Kossel,[6] from the theoretical side, and by K. Spangenberg [7] and his co-workers, from the experimental side. Kossel considers a crystal of the sodium chloride type built up layer by layer, parallel to the cube face. Any given layer is supposed to be built up row by row, and the case is considered of a partly completed layer, resting upon a number of completed ones, which consists of a number of completed rows and one incomplete row. Suppose a new ion is to be added to the structure. It may go to the completed surface so as to start a new layer, it may start a new row immediately beside one already begun, or it may continue the incomplete row. It can be shown that the greatest amount of energy is gained by continuing a row already in existence; next comes the starting of a new row, and last of all, some way behind, the starting of a new layer. Thus there is a marked tendency for a partly-formed cube face to complete itself before a new layer is begun, so that the crystal will grow with plane faces, and the cube form will be much the most probable.

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[3] See a summary by A. Smekal, "Ueber den Aufbau der Realkristalle," *Atti del Congresso Internationale dei Fisici*, Como, 1927. (Volta Centenary.)

[4] *Trans. Faraday Soc.*, 1927, **24**, 53; **A.**, 1928, 111.

[5] *Ibid.*, p. 92; **A.**, 1928, 8.

[6] *Nachr. Ges. Wiss. Göttingen* (*Math.-Phys. Kl.*), 1927 ,135.

[7] *Neue Jahrb. Min.*, B.-Bd., 1927, **57**, 1197.

The actual rate of growth of crystal faces in directions perpendicular to themselves has been measured by K. Spangenberg (*loc. cit.*), and by A. Neuhaus,[8] by a method due originally to D. N. Artemjew,[9] in which a sphere, turned from a single crystal of rock-salt, is suspended in a solution of the same salt, and allowed either to grow, or to dissolve slowly, according to whether the solution is slightly supersaturated, or slightly unsaturated. Great care has to be taken to keep the concentration of the solution constant. The sphere slowly develops faces, ultimately becoming a beautifully regular polyhedron, and the rate of growth of the different faces is compared. With pure sodium chloride solution, the velocities are in the order $v_{110} > v_{210} > v_{111} > v_{100}$, corresponding to a tendency for the actual faces to develop in the order (100), (111), (210), (110). If the solution contains a small quantity of urea, however, the order of velocities is $v_{110} > v_{100} > v_{111}$, corresponding to a tendency for the (111) face to grow at the expense of the others.

The average amplitude of the thermal vibrations, and hence the forces between the atoms, in a crystal lattice may be studied by measuring the variation with temperature of the intensity of reflexion of *X*-rays by the crystal. An important quantity in *X*-ray measurements is the atomic scattering factor—usually denoted by *F*, which is the ratio of the amplitude of the radiation scattered by an atom in a given direction, under the conditions considered, to that scattered in the same direction by a single classically scattering electron; *F* approaches the number of electrons in the atom for small angles of scattering, but falls off in value rapidly with increasing angle, owing to the interference of the waves scattered from different parts of the atom. The greater the volume, therefore, which is occupied by the average atom, the more rapidly does F fall off with increasing angle : it will thus fall off much more rapidly at high temperatures than at low ones, since this volume is greater the greater the amplitude of vibration of the atoms.

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[8] *Z. Krist.*, 1928, **68**, 15.

[9] *Ibid.*, 1918, **48**, 425.

Suppose that $\overline{u^2}$ is the mean-square amplitude of vibration of the atoms of the kind considered, perpendicular to a set of planes in a crystal at which reflexion of X-rays, of wave-length λ, is taking place at a glancing angle θ. Then it has been shown [10, 11] that, if F_0 is the scattering factor of an atom in a state of rest, and F the value for the average atom under the conditions considered, $F = F_0e^{-M}$, where $M = 8\pi^2\sin^2\theta \, . \, \overline{u^2}/\lambda^2$. The value of $\overline{u^2}$ depends, of course, on the interatomic forces, but for certain simple crystals it is possible to calculate it in terms of the elastic constants, and hence, by measuring the dependence of F on temperature, both to check the formula and to estimate the amplitudes of the atomic vibrations.

Measurements of F for a series of spectra from rock-salt [12] and sylvine [13] (KCl) at temperatures ranging from about 86° Abs. to 900° Abs. have shown a very good agreement between the observed values of M and those calculated by Waller, from the lowest temperatures used up to about 500° Abs. At higher temperatures, the intensity of reflexion decreases much more rapidly than theory predicts, but this is to be expected, since the theory is only valid for small amplitudes of vibration. It is really the difference in M at two temperatures which is determined from the ratio of the F values at those temperatures, and it is this difference which is found to agree closely with the values calculated from the elastic constants. If the crystal possesses energy of vibration at the absolute zero, this will correspond to a constant addition to M, which is proportional to the vibrational energy, and this of course cannot be determined from the ratio of F at two temperatures. The new quantum mechanics definitely requires the lattice to possess half a quantum of vibrational energy per degree of freedom at the absolute zero, and, if we assume this amount to be present, we can calculate the actual values of M from the experimental results, and hence the amplitudes of vibration.[14] Furthermore, it is then possible to calculate from the observed values of F_0, the

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[10] P. Debye, *Ann. Physik.*, 1914, **43**, 49.

[11] I. Waller, Dissertation, Upsala, 1925.

[12] R. W. James and (Miss) E. M. Firth, *Proc. Roy. Soc.*, 1927, [*A*], **117**, 62; **A.**, 1928, 225.

[13] R. W. James and G. W. Brindley, *ibid.*, 1928, [*A*], **121**, 155.

[14] I. Waller and R. W. James, *ibid.*, 1927, [*A*], **117**, 214; **A.**, 1928, 112.

values of F for the atoms in a state of rest. Now it will be evident that, if we can calculate the values of F_0 theoretically, we may, by comparing them with those obtained from the experiments, obtain definite information as to the existence of zero-point energy. D. R. Hartree [15] has devised a method for calculating the Schrödinger charge-density distribution, $\psi\bar{\psi}$, for ions such as Na˙, Cl′, and K˙, and it has been shown by Waller that, if this distribution is treated as scattering classically, the correct values of F_0 are obtained. The values of F_0 calculated in this way for Na˙, Cl′, and K˙ agree remarkably closely with those obtained experimentally, and the existence of zero-point energy in rock-salt and sylvine is clearly indicated.[16] The difference between the values of F with and without the correction for zero-point energy is considerable, and should be outside the range of experimental error. The actual values of the root-mean-square amplitude at 17° for the crystals studied are: in KCl, both atoms 0·25 Å.; in NaCl, Na 0·22 Å., Cl, 0·24 Å. The amplitudes of the vibrations at the zero-point are of the order of 0·1 Å. for both crystals.

Experiments of the type just considered have a definite bearing on the problem of determining the structure of the more complex crystals. Unless one is content with the formal determination of the space-group, which is now a nearly mechanical operation, it is necessary to be able to calculate the amount of radiation scattered in different directions by any assumed arrangement of atoms, in order that this can be compared with that actually measured by the spectrometer, or photographic plate. We have in fact a quantitative problem in X-ray optics. The units in terms of which all such calculations must be made are the F factors for the different atoms in the crystal. Experiments on simple crystals such as sodium or potassium chloride show that the quantitative methods rest on a sure foundation, and give one confidence in applying them to more complex cases.[17]

The question of the application of quantitative methods to the analysis of complex crystals has been discussed in detail by W. L. Bragg and J. West.[18] They show that quite a rough *absolute* estimate of F for a large number of spectra leads, even in quite complex cases, to a determination of the parameters of the structure. Working values of the F factors are given for a number of atoms. These are based on a method of calculation due to L. H. Thomas,[19] which, although only approximate, gives results in close enough agreement with those calculated by Hartree to be used in crystal analysis. It must be borne in mind that the intensities of high-order spectra are exceedingly sensitive to small changes in the atomic positions, so that a comparatively rough value of F suffices to fix these with great accuracy. The important thing is that the F values, even if rough, should be absolute values. There are, of course, many difficulties yet to be overcome, particularly those due to the influence of the state of perfection of the crystal on the intensity of reflexion. In this connexion, reference should be made to a very interesting study of the reflexion of X-rays by diamond,[20] and to a paper on the value of F for carbon.[21]

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[15] *Proc. Camb. Phil. Soc.*, 1928, **24**, 89, 111; **A.**, 216.

[16] R. W. James, I. Waller, and D. R. Hartree, *Proc. Roy. Soc.*, 1928, [*A*], **118**, 334; **A.**, 462.

[17] Compare W. L. Bragg, Solvay Conference Report, 1927.

[18] *Z. Krist.*, 1928, **69**, 118.

[19] *Proc. Camb. Phil. Soc.*, 1927, **23**, 542; **A.**, 1927, 290.

There has been a tendency in some quarters to maintain that the legitimate aspirations of X-ray crystallographers should not go beyond the determination of the space-group. It seems difficult to defend this standpoint, and there is little doubt that the technique of crystal analysis is slowly reaching a state in which it will be possible to work out the structures of really complex crystals.

Crystal Structures : (1) Inorganic.

Elements.—The structures of the two forms of manganese have been determined by G. D. Preston,[22] from Laue photographs and rotation photographs. The results obtained for α-manganese confirm the work of Bradley and Thewlis, reported last year. The structure of β-manganese is referred to in connexion with its isomorphism with the alloy Ag_3Al (p. 300).

An allotropic form of silver has been discovered by G. Allard,[23] which is obtained by the action of copper on a solution of silver nitrate; it has an orthorhombic structure.

The alkaline-earth metals have been investigated by G. L. Clark, A. J. King, and J. F. Hyde.[24] Calcium has a face-centred cubic structure, whilst that of barium is body-centred cubic. The structure of strontium is still uncertain, although F. Simon and E. Vohsen [25] assign a face-centred cubic structure to this metal at the ordinary temperature, and a hexagonal close-packed structure at higher temperatures.

The structure of iodine has been investigated by P. M. Harris, E. Mack (jun.), and F. C. Blake,[26] and by A. Ferrari.[27] The elementary cell is an orthogonal parallelepiped with orthorhombic-bipyramidal symmetry, the space group being V_h^{18}. There are eight atoms in the cell, which are grouped in molecules of I_2, the distance between atomic centres being 2·70 Å.

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[20] W. Ehrenberg, P. P. Ewald, and H. Mark, *Z. Krist.*, 1928, **66**, 547.

[21] M. Ponte, *Phil. Mag.*, 1927, **3**, 195; **A.**, 1927, 191.

[22] *Phil. Mag.*, 1928, **5**, 1198, 1207; **A.**, 820.

[23] *Compt. rend.*, 1928, **187**, 223; **A.**, 940.

[24] *Proc. Nat. Acad. Sci.*, 1928, **14**, 617; **A.**, 1177.

[25] F. Simon and E. Vohsen, *Z. physikal. Chem.*, 1928, **133**, 165; **A.**, 694.

[26] *J. Amer. Chem. Soc.*, 1928, **50**, 1583; **A.**, 822.

[27] *Atti R. Acad. Lincei*, 1927, **5**, 582; **A.**, 1927, 611.

Compounds.—In a crystal of ideal type, the unit crystalline cell contains a definite number of atoms. A chemical analysis of such a crystal shows that the law of constant multiple proportions is obeyed, and it is possible to assign to the crystal a formula in which integral numbers of atoms of various types are grouped together. The existence of such a formula has been generally assumed in the *X*-ray analysis of crystals. It is becoming increasingly evident, however, that a cell containing the same integral numbers of each type of atom throughout the crystal represents an ideal state of affairs, to which actual crystals may only approximate, and that wide departures from such a state may be tolerated without destroying the crystalline arrangement, especially in the case of complex types. The deviations may be of a more complicated kind than the well-known partial replacement of atoms of one kind by an equivalent number of atoms similar in chemical nature, or than the replacement in the felspars of the pair Na + Si by the pair Ca + Al.

An interesting case is that of the synthetic spinels examined by F. Rinne.[28] Spinel, $MgAl_2O_4$, crystallises in the cubic system. The magnesium atoms are surrounded by four oxygen atoms at the corners of a tetrahedron, and the aluminium atoms by six oxygen atoms at the corners of an octahedron. These tetrahedra and octahedra are linked together to build up the well-known spinel structure, a classical type, first analysed by W. H. Bragg and H. Nishikawa in 1915. Alumina, Al_2O_3, crystallises in a very different form, with rhombohedral symmetry. Yet the artificial spinels may be made with any proportion of MgO to Al_2O_3 between 1 : 1 (corresponding to the true spinel) and 1 : 5. The crystals show a continuous variation with composition in refractive index and density, and all give almost identical Laue and powder *X*-ray photographs of the spinel type. Rinne concludes that the results may be explained by supposing that the crystals are isomorphous mixtures of spinel with γ-Al_2O_3, a cubic form of alumina, and that their structure may be represented formally as follows :

$$\begin{matrix}\mathrm{MgO\cdot Al_2O_3}\\ \mathrm{MgO\cdot Al_2O_3}\end{matrix} + n\left(\begin{matrix}\mathrm{AlO}\\ \mathrm{AlO}\end{matrix}\mathrm{O}\begin{matrix}\mathrm{Al_2O_3}\\ \mathrm{Al_2O_3}\end{matrix}\right).$$

This case is entirely parallel to the oxidation of magnetite, Fe_3O_4 (with spinel structure), into a cubic form of Fe_2O_3, examined by

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[28] *Neue Jahrb. Min.*, 1928, [*A*], **58**, 43.

O. Baudisch and L. A. Welo,[29] which gives *X*-ray photographs closely similar to those of magnetite. Whatever the precise atomic arrangement may be, it is clear that the unit cells of the two compounds contain different numbers of atoms, and yet that the majority of these atoms are arranged in so similar a way that the *X*-ray patterns are almost indistinguishable, and a wide range of mixed crystals can be formed. The average number of atoms in the unit cell of the mixed crystal is not integral.

In this connexion, it is interesting to discuss the case of sillimanite and mullite. R. W. G. Wyckoff, J. W. Greig, and N. L. Bowen[30] found that powder, Laue, and single-crystal photographs were practically identical for the two compounds, and this was confirmed by J. F. Hyslop and H. P. Rooksby,[31] and by H. Mark and P. Rosbaud.[32] The structure of these compounds has been examined by W. H. Taylor,[33] who sums up the experimental results as follows: (1) Two compounds of quite different composition, sillimanite, Al_2SiO_5,(Al_2O_3,SiO_2), and mullite, $Al_6Si_2O_{13}$,($3Al_2O_3.2SiO_2$), give *X*-ray diffraction data which are almost but not quite identical. (2) The unit cell deduced in the usual way from the mullite data contains only three-quarters of a molecule of mullite ($4\frac{1}{2}$Al,$1\frac{1}{2}$Si,$9\frac{3}{4}$O, atoms).

Taylor has attempted a complete solution of the sillimanite structure, the essential features of which are as follows. The unit cell contains four molecules of Al_2SiO_5. One aluminium, Al(1), and four oxygen atoms of each molecule are used up in forming strings of octahedra, linked together by edges parallel to the *c* axis. The remaining aluminium, Al(2), silicon, and oxygen atoms (one of each) bind the strings together. The binding atoms Al(2) and Si have almost identical *a* and *b* co-ordinates in the structure, and in the *c* direction they alternate at intervals of approximately *c*/2. If the aluminium and silicon atoms are regarded as identical, the whole structure repeats almost exactly at intervals of *c*/2. Hence, in the *X*-ray photographs, the true length of the *c* axis is only shown by certain very weak spots or lines, for Al and Si diffract *X*-rays in a very similar way. The fifth oxygen atom is placed so that the arrangement of oxygen atoms around Al(2) is almost identical with that around silicon.

To compare sillimanite and mullite, it must be noticed that the sillimanite cell contains a group $Al_8Si_4O_{20}$. The mullite cell appears at first sight to have identical *a* and *b* axes, but a *c* axis half as long; however, prolonged exposure in rotation photographs shows that the *c* axes are also identical. The mullite cell thus outlined contains $1\frac{1}{2}$ molecules, *i.e.*, $Al_9Si_3O_{19\frac{1}{2}}$. *X*-Ray data show clearly that the structures are almost identical, and the arrangement of sillimanite indicates the way in which they are related. The positions of Si and Al(2) are so alike that it is easy to understand that one in four of the Si atoms can be replaced by Al, giving Al_9Si_3 in place of Al_8Si_4. Simultaneously, one in every forty oxygen atoms must be removed from the structure, but this would appear to be tolerated without a radical alteration of the general arrangement. The question of the real size of the mullite cell is left open: to satisfy the formal requirements of space-group theory it must be a multiple of that outlined above.

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[29] *Naturwiss*, 1925, **13**, 749. See also *Ber.*, 1928, **61**, 2153, where S. B. Hendricks and W. H. Albrecht discuss the parallel case of the oxidation of CoO,Fe_2O_3 to $Co_2O_3,2Fe_2O_3$.

[30] *Amer. J. Sci.*, 1926, **11**, 459; **A.**, 1926, 664.

[31] *Trans. Soc. Glass Techn.*, 1926, **110**, 412; **B.**, 1927, 219.

[32] *Neue Jahrb. Min.*, 1926, [*A*], **54**, 127.

[33] *Z. Krist.*, 1928, **68**, 503.

To sum up, these cases illustrate a form of isomorphism between compounds in which there is not a one-to-one correspondence between atoms in the formulæ. Of course such isomorphism is indicated by many examples amongst minerals, but it is interesting to see how *X*-ray analysis is tackling the problem of discovering what remains fixed and what is variable in a series of such compounds.

Other interesting cases occur in the silicates. The investigation of a series of sodium and calcium silicates by R. W. G. Wyckoff and G. W. Morey[34] was described in last year's Report, Na_2CaSiO_4 and $Na_4Ca(SiO_3)_3$ being shown to have practically identical *X*-ray diffraction patterns. A very interesting series is that of the artificial ultramarines, investigated by F. M. Jaeger[35,36] and his co-workers. They find for the natural compound nosean a cubic unit cell containing two molecules of $Na_5Al_3Si_3O_{16}S$. Artificial ultramarines, with formulæ approximating to $Na_6Al_4Si_6O_{20}S_4$ (blue), $Na_3Al_4Si_6O_{22}S_3$ (red), and $Na_8Al_6Si_6O_{24}S_2$ (green), all give *X*-ray powder photographs almost identical with those of nosean. The mineral haüyine, ($Na_3CaAl_3Si_3O_{16}S$), also gives the same powder photographs. On the other hand, sodalite, $Na_4Al_3Si_3O_{12}Cl$, gives quite a different pattern.

A repetition by R. W. G. Wyckoff and S. B. Hendricks[37] of the analysis of zircon, $ZrSiO_4$, is of interest because the simplicity of the structure makes it possible to determine the situations of the oxygen atoms around the silicon atoms with high accuracy. Zirconium and silicon atoms are fixed in position by the symmetry requirements of the tetragonal lattice. The accuracy estimated for the two parameters u and v determining the positions of the oxygen atoms is shown by the limits

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[34] *Amer. J. Sci.*, 1926, [v], **12**, 419; **A.**, 1927, 10.

[35] F. M. Jaeger, G. K. Westenbrink, and F. A. van Melle, *Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30**, 249; **A.**, 1927, 715.

[36] F. M. Jaeger and F. A. van Melle, *ibid.*, p. 885; **A.**, 1928, 463.

[37] *Z. Krist.*, 1927, **66**, 73; **A.**, 1928, 821.

$$0{\cdot}18<u<0{\cdot}20;\ 0{\cdot}32<v<0{\cdot}34.$$

The upper limits are estimated to be most probable. It follows from this, that oxygen atoms build a regular tetrahedron around the silicon atoms with a silicon–oxygen distance of 1·64 Å., and an oxygen-oxygen distance of 2·64 Å. These results confirm those of earlier observers. L. Vegard[38] in 1926 found (in Wyckoff's notation) $u = 0{\cdot}190$ and $v = 0{\cdot}306$. Wyckoff states that his results do not agree with those of Vegard, but the latter points out[39] that this apparent disagreement is due to a different choice of crystal axes. W. Binks[40] with the aid of spectrometer measurements found $u = 0{\cdot}212$, $v = 0{\cdot}333$.

The structure of diopside[41] throws light on the pyroxene–amphibole series of minerals. Diopside is a typical pyroxene. The monoclinic cell contains four molecules of $CaMg(SiO_3)_2$. Each silicon atom is surrounded by four oxygen atoms at the corners of a regular tetrahedron, the average Si–O distance being 1·61 Å. One edge of the tetrahedron is nearly parallel to the c axis, and the oxygen atoms at each end of this edge are common to two tetrahedra. The tetrahedral groups thus form a series of endless chains parallel to the c axis of the crystal. These chains lie side by side and are cemented together by the calcium and magnesium atoms. The three typical cleavages of the crystal are parallel to the chains, evidence of the relatively high strength of binding along the chains. This would appear to throw light on the structure of fibrous minerals such as asbestos (an amphibole) where the fibre direction corresponds to the c axis of diopside.

In a paper on the felspars, F. Machatschki[42] proposes a division of the silicates into three main types, which is novel and suggestive. It is known that oxygen atoms are grouped in fours around silicon and beryllium, probably also around boron and, in certain cases, aluminium. Machatschki considers the linking up of these tetrahedral groups. In the orthosilicates proper ("Ortho-typus"), there are separate tetrahedral groups enclosing silicon atoms, an example being Mg_2SiO_4. It is supposed, on the other hand, that in the

[38] *Phil. Mag.*, 1926, **1**, 1151; **A.**, 1926, 663.

[39] *Z. Krist.*, 1928, **67**, 482.

[40] *Min. Mag.*, 1926, **21**, 176.

[41] B. Warren and W. L. Bragg, *Z. Krist.*, 1928, **69**, 168.

[42] *Zentr. Min. Geol.*, 1928, [*A*], **3**, 97; **A.**, 1349.

felspars ($NaAlSi_3O_8$; $CaAl_2Si_2O_8$), aluminium as well as silicon lies between four oxygen atoms. There is one atom of silicon or aluminium to every two atoms of oxygen; hence a tetrahedral group must share each corner with a neighbouring group, just as in quartz, SiO_2. He names this class the " Feldspat-typus," and remarks that all forms of SiO_2, and the crystals beryl and phenacite, belong to it. (Beryl has the formula of a metasilicate, and phenacite that of an orthosilicate.) Finally, he supposes an intermediate type (" Meta-typus ") to exist, in which the ratio of kations inside tetrahedra to anions is 1 : 3. In this case, the tetrahedra are linked in chains, each group holding two oxygen atoms in common with its neighbours. It is interesting to note that this structure has actually been discovered in diopside.

Two determinations[43, 44] of the structure of topaz, $[Al(F,OH)]_2SiO_4$, are in complete agreement as regards the general arrangement of atoms. The structure is described by Alston and West as an arrangement of oxygen and fluorine atoms in closest packing. It is interesting because the packing is not either of the well-known cubic or hexagonal forms, but has features common to both. A similar arrangement has been noticed by L. Pauling in the structure of brookite (see below). In all forms of closest packing, sheets of oxygen atoms are packed one on top of the other, but whereas in the hexagonal closest packing the third layer, and in the cubic closest packing the fourth layer, repeats the position of the first, in this new type it is the fifth layer which does so. Silicon atoms lie between four oxygen ions, and aluminium atoms between four oxygen ions and two fluorine or hydroxyl ions. The positions of all atoms in the structure were verified by direct *X*-ray analysis.

An identical structure is arrived at by Pauling, who bases his arrangement on the general features of co-ordination compounds.* He develops an interesting method of investigating the structure of these compounds. The investigations of a number of workers have shown that co-ordination compounds may be regarded as fabrics composed of regular arrangements of the anions around the kations, the most common grouping being four anions at the corners of a tetrahedron, or six at the corners of an octahedron. In the silicates in particular, the common groupings are those of four oxygen atoms around Si and Be, possibly also B, and of six oxygen atoms around Al: either group occurs around such atoms as Mg or Fe. By a sharing of oxygen atoms between groups, continuous structures are built up, like fabrics of which tetrahedral and octahedral groups are the individual stitches. Pauling uses this feature to suggest possible structures for complex ionic compounds, and tests the possibilities by *X*-ray analysis. For instance, in topaz, he assumes that aluminium is surrounded by six anions and silicon by four anions, as in other silicates. He then treats these octahedral and tetrahedral groups as units, and, by trying various ways of fitting them together, discovers one which has the same symmetry as topaz, and which explains the main features of its *X*-ray diffraction patterns.

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* The word " co-ordination " is here used, in the sense common in *X*-ray analysis, as designating an arrangement which may be regarded as a continuous structure of oppositely charged ions.

[43] L. Pauling, *Proc. Nat. Acad. Sci.*, 1928, **14**, 603; **A.**, 1176.

[44] N. A. Alston and J. West, *Proc. Roy. Soc.*, 1928, [*A*], **121**, 358; *Z. Krist.*, 1928, **69**, 149.

This method of investigating the structures of compounds had previously been outlined by Pauling [45] in a paper on the structure of brookite, TiO_2, which affords a very interesting example of polymorphism. The structures of rutile and anatase, other forms of TiO_2, have been known for some time. In both cases the titanium atom is surrounded by six oxygen atoms at the corners of a distorted octahedron. Pauling assumes a similar arrangement of the oxygen atoms around the titanium atoms in brookite. By trying various ways of fitting the octahedra together, one is found which appears to be the brookite structure. Each octahedron shares three edges with neighbouring octahedra. Eight octahedra are contained in the orthorhombic unit cell with the space group V_h^{15}, and the main features of the *X*-ray diffraction pattern are explained.

The regarding of co-ordination compounds as composed of linked tetrahedral and octahedral groups of anions is not novel; it is a very striking feature which has often been stressed in describing these compounds. Pauling has, however, extended the idea further by considering both the nature of the linking (corner-, edge-, or face-shared) and the distortion from the regular form, and has developed a most promising method of investigating complex crystals.

A very interesting paper by W. H. Zachariasen [46] forms one of a series coming from Prof. V. M. Goldschmidt's laboratory at Oslo. It deals with the whole series of sesquioxides and compounds of the type ABO_3. The value of such surveys is considerable, because the ground is so completely covered. Most of the sesquioxides belong either to the corundum (Al_2O_3) type or to a new type (*C*-type), of which Mn_2O_3 is an example. The calcite, aragonite, and perowskite structures are repeated by many of the ABO_3 compounds. Special structures are found for $AgNO_3$, $RbNO_3$, $KClO_3$, HIO_3, $AgClO_3$, and are completely or partly analysed.

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[45] L. Pauling and J. H. Sturdivant, *Z. Krist.*, 1928, **68**, 239

[46] *Norske Vid. Akad.*, Oslo, 1928, No. 4.

The structure of potassium dihydrogen phosphate has been examined by S. B. Hendricks.[47] The symmetry is tetragonal-scalenohedral. Potassium and phosphorus atoms are at positions fixed by symmetry, and oxygen atoms in positions fixed by three co-ordinates, as reported by O. Hassel.[48] The positions of the oxygen atoms could only be fixed within rather wide limits

$$(0{\cdot}045<x<0{\cdot}075;\ 0{\cdot}120<y<0{\cdot}135;\ 0{\cdot}145<z<0{\cdot}165).$$

Allowing for the full variation of position within these limits, however, the assigned structure gives a tetrahedral arrangement of oxygen atoms which is much distorted from the regular form. The O–O distance in a group is between 1·92 and 2·20 Å., parallel to the plane (001), and is 2·62—2·81 Å. along the other edges of the tetrahedron. This big distortion is significant, particularly with regard to the possible influence of the hydrogen atoms, and raises an interesting point.

An investigation of alum by L. Vegard and E. Esp[49] links up with a previous investigation by J. M. Cork.[50] The positions of the atoms (excluding hydrogen) are fixed by eleven parameters, and the structure is partially analysed. In agreement with previous work, four molecules of $KAl(SO_4)_2,12H_2O$ are found in the unit cell, with symmetry T_h^6, and potassium and aluminium in the Na and Cl positions of rock-salt. Vegard and Esp further find a position for the sulphur atom which agrees with that found by Cork, and suggest an orientation of the SO_4 group which corresponds with one alternative indicated by Cork's results. The authors stress the speculative nature of their conclusions, and further work on this interesting structure is clearly necessary.

Complex Salts.—As the study of the structure of complex salts proceeds, we see how essentially correct are the ideas of Werner on co-ordination, and those of V. M. Goldschmidt on the determination of structures by the size and polarisation properties of their component units (see *Ann. Report*, 1927, **24**, 274). The structures in all cases so far investigated are those where the ions of simple salts have been replaced by complex (co-ordination) ions.

This, in general, leads to high symmetry—in some cases even to a higher symmetry than that possessed by the complex ion itself. O. Hassel[51] has shown that not only are crystals of the pentammino-aquo-type, $[Co(NH_3)_5,H_2O]I_3$ or $[Co(NH_3)_5,H_2O](ClO_4)_3$, isomorphous with those of the corresponding hexammino-compounds, $[Co(NH_3)_6]I_3$

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[47] *Amer. J. Sci.*, 1927, **14**, 269; **A.**, 1927, 1013.

[48] *Z. Elektrochem.*, 1925, **31**, 513; *A.*, 1925, ii, 1130.

[49] *Ann. Physik*, 1928, **85**, 1152; **A.**, 820.

[50] *Phil. Mag.*, 1927, (vii), **4**, 688; **A.**, 1928, 6.

[51] *Norsk. Geol. Tidskr.*, 1928, **9**, 33; **10**, 92.

or $[Co(NH_3)_6](ClO_4)_3$ (see Report for 1927), but also that they have the same cells, and are indistinguishable, except for a small change in the spacing. It is impossible for such a group as $Co(NH_3)_5,H_2O$ to have any form of cubic symmetry, so that there is a contradiction of the law that equivalent crystallographic positions must be occupied by identical atoms. The contradiction is only apparent, for we may assume either that the cell is really much larger, in a way undetectable by X-rays owing to the inappreciable difference of scattering power between O and N, or that the $Co(NH_3)_5,H_2O$ groups take up all different orientations in a fortuitous manner, giving rise to what might be called a statistically symmetrical or self-mixed crystal. That there is no appreciable loss of symmetry is shown by the optical isotropy of the crystals. A similar state of affairs was shown to exist in the newly investigated series :

$[Co(NH_3)_6]^{I}_{SO_4}$, $a = 10{\cdot}71$ Å. $[Co(NH_3)_5,H_2O]^{I}_{SO_4}$, $a = 10{\cdot}62$ Å.

$[Co(NH_3)_6]^{Br}_{SO_4}$, $a = 10{\cdot}51$ Å. $[Co(NH_3)_5,H_2O]^{Br}_{SO_4}$, $a = 10{\cdot}45$ Å.

$[Co(NH_3)_6]^{I}_{SeO_4}$, $a = 10{\cdot}79$ Å.

which has a fluorite structure with $Co(NH_3)_6^{\cdot\cdot\cdot}$ in the place of $Ca^{\cdot\cdot}$, and SO_4'' and I' alternately in the place of $2F'$.

When the complex ion is more polarisable, there is the usual loss of symmetry. Thus $K_2Sn(OH)_6$, investigated by R. W. G. Wyckoff,[52] has a rhombohedral cell containing one molecule, and resembles the K_2SnCl_6 structure compressed along one trigonal axis. In $K_2Pt(SCN)_6$, as S. B. Hendricks and H. E. Merwin[53] have shown, the distortion is still greater and the structure resembles cadmium iodide rather than fluorite. Isomorphous structures were found for the rubidium and ammonium salts. A similar loss of symmetry is produced by an unsymmetrical kation. In $(CH_3{\cdot}NH_3)_2SnCl_6$ and $(C_2H_5{\cdot}NH_3)_2SnCl_6$, investigated by Wyckoff,[54] the former has a pseudocubic rhombohedral cell containing one molecule, resembling $(NH_4)_2SnCl_6$ but elongated along one trigonal axis, and the latter has a hexagonal cell containing one molecule with an anti-cadmium iodide structure. The full atomic parameters have been determined in none of these cases, but the interatomic distances are in accord with those of better-known crystals.

Water of Crystallisation.—Two interesting hydrated salts, lithium chloride monohydrate and lithium iodide trihydrate, have been investigated by S. B. Hendricks.[55] In neither case was an unambiguous structure found, on account of the small scattering of the Li ions, but the proposed structures are very plausible on other grounds. $LiCl,H_2O$ is tetragonal with a pseudocubic cell, $a = 3{\cdot}83$, $c = 3{\cdot}88$ Å., with one molecule, and has a cæsium chloride structure, the large $Cs^{\bullet}$ ion being replaced by the complex $LiOH_2^{\bullet}$ ion, hydrogen atoms not being considered in the symmetry. $LiI,3H_2O$ is hexagonal: $a = 7{\cdot}45$, $c = 5{\cdot}43$ Å. with two molecules in the cell, and is isostructural with triethylammonium iodide (see below), the complex $Li(OH_2)_3^{\bullet}$ replacing $NHEt_3^{\bullet}$.

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[52] *Amer. J. Sci.*, 1928, **15**, 297; **A.**, 463.

[53] *Ibid.*, p. 487; **A.**, 820.

[54] *Ibid.*, 1928, **16**, 349; **A.**, 1176; *Z. Krist.*, 1928, **68**, 231.

Salts of the Substituted Ammonias.—Our knowledge of these salts is mainly due to the work of Wyckoff and Hendricks, which has furnished results of great theoretical importance. When groups of higher alkyls are substituted in the ammonium radical, a continuous transition of structure and properties between inorganic and organic crystals is observed. So far, the salts investigated fall into three groups: (1) the symmetrical tetra-alkylammonium salts $(NR_4)X$, where R is an alkyl radical and X a halogen, (2) the monoalkylammonium salts $(NH_3R)X$, and (3) the symmetrical trialkylammonium salts $(NHR_3)X$.

(1) Of these, tetramethylammonium iodide has been most studied.[56] Apart from the early investigations of Vegard, all the workers agree as to the main details of the structure, a simple tetragonal cell $a = 7{\cdot}94$ Å., $c = 5{\cdot}75$ Å., space-group D_{4h}^{7}, containing two molecules. G. Greenwood found a different space group, D_{2d}^{3}, but this may be due to wrong indexing of planes; however, the class D_{2d} still remains a possibility. The structure is similar to that of phosphonium iodide, and is a distorted version of that of ammonium chloride (cæsium chloride structure). The chloride and bromide differ from the iodide only in having a slightly smaller cell. The structure of tetraethylammonium iodide is much less certain, since the three different investigators [57] only agree as to the cell, $a = 8{\cdot}85$ Å., $c = 6{\cdot}93$ Å., with two molecules, and the face-centred arrangement of the iodine atoms. The symmetry found by Wyckoff is D_{2d}, while I. Nitta finds no symmetry planes in the Laue photographs, indicating an S_4 symmetry. The differences between these results show that it is unsafe to draw far-

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[55] *Ibid.*, 1927, **66**, 297; *Amer. J. Sci.*, 1928, **15**, 403; **A.**, 694.

[56] L. Vegard, *Phil. Mag.*, 1917, **33**, 395; *Vides. Akad. Oslo*, 1926, No. 10; G. Greenwood, *Min. Mag.*, 1927, **21**, 258; **A.**, 1928, 108; R. W. G. Wyckoff, *Z. Krist.*, 1928, **67**, 91; W. Zachariasen, *Norsk. Geol. Tidsskr.*, 1927, **10**, No. 1; *Chem. Zentr.*, 1928, i, 1360; **A.**, 940.

[57] G. Greenwood, *loc. cit.*; R. W. G. Wyckoff, *Z. Krist.*, 1928, **67**, 550; I. Nitta, *Proc. Imp. Acad., Tokyo*, 1928, **4**, 292; **A.**, 1079.

reaching conclusions from them at the present time. However, the structure is obviously of the anti sodium-chloride type.

(2) The great majority of monoalkylammonium salts [58] are found to conform to a tetragonal distorted sodium chloride, cæsium chloride, or anti sodium-chloride structure, as would be expected with a kation of increasing size. The cell dimensions are shown in Table I. (The *a* axes corresponding to the pseudo-cubic structure of the NaCl types are shown; the true *a* axes are $1/\sqrt{2}$ of these.)

TABLE I.

Salt.	*a*.		*c*.		Structure.	Diff. per C atom in *c*-axis.
NH_4Cl	3·86		3·86		CsCl	
NH_4I		7·58		7·58	CsCl	
$CH_3{\cdot}NH_3Cl$	4·28		5·13		CsCl	1·27
$CH_3{\cdot}NH_3Br$		7·10		8·75	NaCl	
$CH_3{\cdot}NH_3I$		7·24		8·95	NaCl	1·37
	c.	*b*.	*a*.	*β*.		
$C_2H_5{\cdot}NH_3Br$	4·63	6·24	8·32	86° 59′	Monoclinic	
$C_2H_5{\cdot}NH_3I$	4·81	6·63	8·68	87° 54′	,,	
$C_3H_7{\cdot}NH_3Cl$	4·48		7·40		CsCl	$(1{\cdot}14) = \frac{2{\cdot}27}{2}$
$C_3H_7{\cdot}NH_3Br$	4·57		7·36		CsCl	
$C_3H_7{\cdot}NH_3I$	4·85		7·33		CsCl	
$C_4H_9{\cdot}NH_3Cl$		7·10		14·85	Anti-NaCl	
$C_4H_9{\cdot}NH_3Br$		7·10		15·23	,,	
$C_4H_9{\cdot}NH_3I$		7·33		15·30	,,	
$C_5H_{11}{\cdot}NH_3Cl$		7·09		16·69	,,	1·84
$C_5H_{11}{\cdot}NH_3Br$		7·09		16·95	,,	1·72
$C_5H_{11}{\cdot}NH_3I$		7·25		17·20	,,	1·90
$C_6H_{18}{\cdot}NH_3Cl$		7·05		19·55		2·86
$C_6H_{13}{\cdot}NH_3Br$		6·96		19·78		2·83
$C_6H_{13}{\cdot}NH_3I$		7·29		19·54		2·34
$C_7H_{15}{\cdot}NH_3Cl$		7·02		21·09		1·54
$C_7H_{15}{\cdot}NH_3I$		7·31		21·14		1·60

Apart from the beautiful manner in which this series demonstrates the ideas of ionic dimensions, the chief interest lies in the latter half of the table, where all the salts have the same anti sodium-chloride structure. Here it can be seen that the *c*-axis increases progressively, although apparently by very different steps, with each additional carbon atom, and it is plain that the general direction of the carbon chain lies along the *c*-axis. This raises a very important point. If the cell and space group D_{4h}^{7} are correct, the only possible positions for the carbon atoms are along tetrad axes, implying a straight carbon chain with a mean distance C–C of 1·3 Å. On the other hand, in all other compounds a C–C distance of 1·4—1·55 Å. has been found, and there is the strongest evidence for zigzag chains in the higher paraffins (see below). Hendricks' assertion that the chain must be straight conflicts with a large body of other evidence, and the question whether it necessarily follows from his data must be examined. The carbon chain can be proved straight only if (*a*) the crystal is tetragonal, (*b*) the crystal is ideally and not statistically symmetrical (see above; complex salts), and (*c*) the cell size is correctly known. Of these conditions the first two are on general principles the easiest to verify, but to establish the third would require much more refined methods. Hendricks himself states that in estimating intensities the contributions of the carbon atoms can be neglected. *A fortiori* intensities, and with them the cell and space-group derived from the absence of reflexions from planes of multiple spacing, cannot be used to fix the carbon atom positions. The weak additional spots, and small changes in intensity of the observed spots due to a zigzag carbon chain, could probably only be detected by careful ionisation spectrometer work. The evidence so far may be said to confirm the arrangement of carbon atoms in rows in the shorter aliphatic chains, but not to determine their detailed structure.

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[58] S. B. Hendricks, *Z. Krist.*, 1928, **67**, 106, 119, 465; **68**, 189.

(3) Triethylammonium chloride[59] has a hexagonal cell $a = 8{\cdot}38$ Å., $c = 7{\cdot}74$ Å., space group C_{6v}^{4}, with two $NH(C_2H_5)_3Cl$ molecules. The three ethyl groups are arranged almost in a plane, with the nitrogen atom in the centre. Each halogen atom is surrounded by three triethylammonium groups in the same plane, and by one above and below, and *vice versa* for the ammonium group, forming an interesting 5—5 co-ordination arrangement (as mentioned above, this is also the structure of $LiI,3H_2O$).

Crystal Structures : (2) *Organic Compounds.*

In the past year, the three main problems in the crystal structure of organic compounds, *viz.*, the symmetry of the carbon atom, the nature of the aliphatic chain, and that of the aromatic ring, have been brought almost to the point of solution.

Symmetry of the Carbon Atom.—The controversy, alluded to in last year's Report, between the advocates of a pyramidal and those of a tetrahedral bisphenoidal arrangement of the four substituted groups around a carbon atom has been satisfactorily settled in favour of the latter, all pyramidal arrangements so far suggested having proved to be of a bisphenoidal nature. The careful crystallographic work of H. Seifert,[60] and the researches of A. Hettich and A. Scheede[61] into pyro- and piezo-electrical properties, have shown that the symmetry of pentaerythritol itself is most probably S_4, and that the apparent electrical polarity is simply due to the absence of a centre of symmetry. Pentaerythritol tetra-acetate and tetranitrate were investigated by A. Gerstäcker, H. Möller, and A. Reis,[62] using a Weissenberg moving-film camera, which separates very beautifully the reflexions of planes which might be confused on an ordinary rotation photograph. The tetra-acetate, $C(CH_2{\cdot}O{\cdot}OC{\cdot}CH_3)_4$, was found to have a tetragonal cell, $a = 12{\cdot}34$ Å., $c = 5{\cdot}56$ Å., with two molecules, and was assigned the space group C^3_{4h}, which left the possibility of a pyramidal C_4 molecule. This conclusion, however, was disproved by (Miss) I. E. Knaggs,[63] who showed that the (001) reflexion previously found was spurious, and that the true space group was C^4_4, giving a bisphenoidal molecular symmetry S_4; and her interpretation was subsequently accepted by the original authors. The tetranitrate, $C(CH_2{\cdot}NO_3)_4$, has a tetragonal cell $a = 9{\cdot}45$ Å., $c = 6{\cdot}74$ Å., space group D^4_{2d}, with two molecules, giving a molecular symmetry S_4.

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[59] S. B. Hendricks, *Z. Krist.*, 1928, **67**, 472.

[60] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1927, 289; **A.**, 1928, 351.

[61] *Z. Physik*, 1927, **46**, 147; **A.**, 1928, 351.

The structure of several ethane substitution products has been carefully studied by Mrs. Lonsdale (Miss K. Yardley).[64] All are of low symmetry, and the success of the investigation depended on the use of intensities measured by the ionisation spectrometer, rather than on the purely photographic methods which have been used with most organic crystals. The first isomorphous series investigated contained the substances C_2Cl_6,C_2Br_6,$C_2Cl_4Br_2$ (two forms), C_2Br_5F,$C_2Cl_3Br_3$ and $C_2Br_4(CH_3)_2$ (two forms, one obtained below 0°). All have orthorhombic cells ($a = 10{\cdot}5$—$12{\cdot}0$, $b = 10{\cdot}1$—$10{\cdot}9$, $c = 6{\cdot}4$—$6{\cdot}7$ Å.), space group V^{16}_h, with four molecules. Each molecule has one plane of symmetry passing through the two carbon atoms, and a pseudo-symmetry centre. Less complete determinations were made of the tetragonal forms $CMeBr_2{\cdot}CMeBr_2$ and $CMe_2Br{\cdot}CMe_2Br$, and of the pseudo-tetragonal tertiary alcohol $CMe_3{\cdot}CMe_2{\cdot}OH$. The cell dimensions of the first two are $a = 8{\cdot}81$ Å., $c = 11{\cdot}27$ Å., and $a = 10{\cdot}45$ Å., $c = 8{\cdot}14$ Å., respectively, each containing four molecules. It can be seen that the crystals though isostructural are by no means isomorphous. In both crystals the substituent atoms or radicals arrange themselves in an octahedron about the two central carbon atoms, it being impossible to determine the relative positions of these in the molecule. These difficulties are essentially similar to those encountered in dealing with the substituted ammonias (see above).

The whole question of the crystallographic and other evidence for the spatial distribution of the valencies of the carbon atom is fully discussed by Mrs. K. Lonsdale [65] in a paper entitled " Evidence of the Anisotropy of the Carbon Atom." She concludes that the carbon atom has two different types of valency, denoted by A and B, and associated conjecturally with the electron orbits (2_1) and (2_2). A C–C bond is always formed of an A valency from one atom with a B valency from the other. In this way she explains the structures of diamond, graphite, the ethane derivatives, and the benzene ring. As expounded in this paper, the idea of A and B valencies, though very suggestive, will not meet the rigid requirements of the recent application of the wave mechanics to chemical combination as developed by W. Heitler and F. London.[66] It may, however, be possible to restate Mrs. Lonsdale's ideas in terms of wave mechanics while conserving their undoubted relation to crystal structure. J. C. McLennan and W. G. Plummer [67] have made a preliminary announcement of the determination of the structure of methane. The cell is cubic, face-centred with four molecules, thus resembling the argon structure, as would have been expected. The important question of the distribution of hydrogen atoms in the molecule will probably prove too difficult for X-ray determination.

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[62] *Z. Krist.*, 1928, **66**, 355; **A.**, 1177.
[63] *Nature*, 1928, **121**, 616; **A.**, 464.
[64] (Miss) K. Yardley, *Proc. Roy. Soc.*, 1928, [*A*], **118**, 449, 485; **A.**, 575.
[65] *Phil. Mag.*, 1928, **6**, 433; **A.**, 1079.

Aliphatic Compounds.—In the past year A. Müller [68] has extended his researches into long-chain compounds by an investigation of a single crystal of the paraffin $C_{29}H_{60}$. This has proved to have an orthorhombic cell, $a = 7{\cdot}45$, $b = 4{\cdot}97$, $c = 77{\cdot}2$ Å., containing four molecules, space group V_h^{16}. The carbon chains are here perpendicular to the (001) cleavage planes, and not inclined to them as in most other aliphatic types. By careful quantitative studies of the intensities, which were made possible by the use of the Astbury integrating photometer, the positions of the carbon chains could be approximately fixed, and the zigzag arrangement was confirmed in this case also. The following numerical data are the most exact yet obtained in long-chain compounds :

Mean distance S between alternate carbon atoms = 2·54 Å.
Zigzag angle = 84°
Mean C–C distance = 1·9 Å.
Cross-section area of CH_2 chain = $18{\cdot}5 \times 10^{-16}$ sq. cm.

Still higher hydrocarbons have been studied by J. Hengstenberg.[69] He obtains the following cells :

	a.	*b*.	*c*.	Distance, *S*.
$C_{35}H_{72}$	7·43	4·97	92·4	2·5
$C_{60}H_{122}$	7·44	4·95	156·4	2·54
$C_{80}H_{162}$	7·44	4·95	—	2·54

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[66] W. Heitler and F. London, *Z. Physik*, 1927, **44**, 455; **A.**, 1927, 923.

[67] *Nature*, 1928, **122**, 571.

[68] *Proc. Roy. Soc.*, 1928, [*A*], **120**, 437; **A.**, 1176.

[69] *Z. Krist.*, 1928, **67**, 583.

in very good agreement with Müller's values. For the highest hydrocarbon, the orders of the (001) planes cease to be distinguishable. An investigation by R. Brill and K. Meyer[70] of the acid $C_{11}H_{23}{\cdot}CO_2H$ gives a cell $a = 9{\cdot}76$, $b = 4{\cdot}98$, $c = 36{\cdot}9$ Å., $\beta = 48° 6'$, with four molecules, in accord with the structures of other monobasic fatty acids.

Our knowledge of aliphatic compounds is much hindered by the fact that the lower members of most series exist in the liquid state at the ordinary temperature. Important information has, however, been gained by the study of *X*-ray scattering in liquids. In a series of papers, G. W. Stewart, E. W. Skinner, and R. M. Morrow[71] give the results of an examination, by means of an ionisation spectrometer, of the scattering from a series of primary normal alcohols, isomeric normal alcohols, monobasic fatty acids, and paraffins with from one to eleven carbon atoms. All except the last show two scattering maxima, corresponding to the main and side spacings of the solid long-chain compounds. The former increases more or less regularly with the carbon content, whilst the latter remains approximately constant, except in the lowest members. The isomeric alcohols gave shorter main and longer side spacings than their corresponding normal alcohol, as might be expected. The paraffins gave only side spacings, owing probably to the lack of a definite group to mark the end of the molecule. It is interesting to note that, in the case of the acids, the long spacings are consistently shorter in the liquid than in the solid phase.

These results, as well as those of F. Zernike and J. A. Prins[72] and of C. V. Raman[73] and C. M. Sogani,[74] all agree with what is known about the higher members of aliphatic series, and extend our knowledge by inference to the lowest members. Already this new branch of *X*-ray investigation has shown its usefulness. Whether or no the diffraction by liquids indicates the existence in the liquid of an incipient crystalline or cybotactic state is more doubtful, as the maxima may be simply due to a random distribution of molecules of definite shape and polarity. Such molecules, if they are to be as close packed as the density of the liquid demands, must form groups throughout which they lie approximately parallel to each other like sheep in a narrow pen, but such associations need neither be extensive nor more than instantaneous to produce the observed *X*-ray pattern, as Debye has shown.

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[70] *Z. Krist.*, 1928, **67**, 570.

[71] G. W. Stewart and R. M. Morrow, *Proc. Nat. Acad. Sci.*, 1927, **13**, 222; **A.**, 1927, 612; *Physical Rev.*, 1927, **30**, 232; **A.**, 1927, 1015; G. W. Stewart and E. W. Skinner, *ibid.*, 1928, **31**, 1, 174; **A.**, 465; R. M. Morrow, *ibid.*, p. 10; **A.**, 224.

[72] *Z. Physik.*, 1927, **41**, 184; **A.**, 1927, 295.

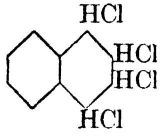
[73] *Nature*, 1927, **119**, 601; **A.**, 1927, 499; *ibid.*, **120**, 514; **A.**, 1927, 1015.

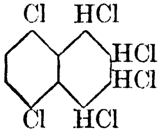
[74] *Indian J. Physics*, 1927, **1**, 357; **A.**, 1927, 924.

Aromatic Compounds.—A further important stage in the solution of the benzene-ring problem is marked by the analysis of the structure of solid benzene by E. G. Cox,[75] of which a preliminary account has appeared. The cell is orthorhombic, $a = 7{\cdot}44$, $b = 9{\cdot}65$, $c = 6{\cdot}81$ Å. at 22°, and the space group V_h^{15}, with four molecules. The benzene molecule is shown to possess only a centre of symmetry. Equally important is a preliminary announcement of the structure of hexamethylbenzene by Mrs. Lonsdale.[76] This triclinic crystal has one molecule in the cell, with only a centre of symmetry. The molecule lies in the *ab* plane, and has a well-marked pseudo-hexagonal symmetry. The molecules are apparently flat, and the molecular sheets are separated by a distance of 3·4 Å. The completion of these researches will be very interesting.

J. M. Robertson [77] has carried out a very careful photographic investigation of two naphthalene derivatives, *viz.*, 1 : 2 : 3 : 4-tetrachloro-1 : 2 : 3 : 4-tetrahydronaphthalene (I) and 1 : 2 : 3 : 4 : 5 : 8-hexachloro-1 : 2 : 3 : 4-tetrahydronaphthalene (II). Both structures

(I.)





(II.)

are essentially similar to that of naphthalene, the double rings lie in the *ac* planes and are probably flat, with the halogen atoms in between.

Two *cyclo*hexane derivatives, β-benzene hexabromide and hexachloride, have been investigated by R. G. Dickinson and C. Bilicke.[77a] The symmetry is cubic T_h^6 with four molecules in the cell. The molecules have centres of symmetry and trigonal axes. The high symmetry enables the carbon and halogen atoms all to be determined by three parameters each. Unfortunately only the halogen atoms can be definitely fixed; they lie on a puckered hexagon of 3·4 Å. side. The carbon atoms probably lie on another puckered hexagonal ring and can be fitted on to one whose angles are all nearly tetrahedral. The puckering of the ring and the symmetry higher than that of the corresponding hexabromobenzene are probably correlated to the change from benzenoid to paraffin linkage.

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[75] *Nature*, 1928, **122**, 401; **A.**, 1081.

[76] *Ibid.*, p. 810.

[77] *Proc. Roy. Soc.*, 1928, [*A*], **118**, 709; **A.**, 574; (Sir) W. H. Bragg, *Z. Krist.*, 1927, **66**, 22; **A.**, 1928, 940.

[77a] *J. Amer. Chem. Soc.*, 1928, **50**, 764; **A.**, 465.

Cellulose Derivatives.—*X*-Ray methods are proving to be of great use in investigating the more complicated natural organic compounds. Of these, cellulose has been most studied, and its structure has at last been elucidated, at least qualitatively. In a most interesting paper K. H. Meyer and H. Mark [78] review the whole subject of cellulose and its derivatives.

The cell of natural cellulose, as shown by its fibre diagram, has the following dimensions :

$$a = 8{\cdot}7\ \text{Å.},\ b = 10{\cdot}3\ \text{Å.},\ c = 7{\cdot}8\ \text{Å.},\ \beta = 90°,$$

the most probable space group C_2^2 containing four molecules of "Glucose residue." It is suggested that these molecules are not separate, as in a molecular crystal, but are joined by a glucoside link through hydroxyl groups in the *b* direction (which is the fibre axis) so as to form long-chain molecules held together at the sides by ordinary molecular forces. This would make cellulose an example of continuous linkages in one dimension, just as graphite and diamond linkages extend in two and three dimensions respectively. Mercerisation, nitration, and other chemical processes have been shown not to affect the structure essentially, but only to alter the cell size and change the relative intensities of reflexion in a reversible way. This is because the substituent groups attack only the sides of the chain, without breaking the chains themselves. The high molecular weight of cellulose would, according to this explanation, refer not to the molecule but to the fibrous crystallites, which retain their structure even in solution. Similar explanations may be found to account for the structure and properties of most other fibrous organic substances, such as silk and chitin, and also for such substances as bakelite and other hard organic condensation products, where the homopolar links extend in all three dimensions.

Crystal Structures : (3) *Alloys.*

Many *X*-ray investigations on alloys have been reported during the past twelve months, and a considerable amount of new light has been shed on the chemistry of these substances. From the point of view of *X*-ray work, alloys may be divided into three classes : (1) Solid solutions which are characterised by random replacement of the parent atoms by the substituent atoms. (2) Inter-metallic compounds, in which the atoms of different kinds occupy fixed positions in the structure. (3) Solid solutions which are characterised by interstitial replacement.

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[78] *Ber.*, 1928, **61**, [*B*], 593; **A.**, 621.

The first category of alloys has recently been the subject of some important quantitative investigations. L. Vegard [79] has shown that certain apparent exceptions to the laws of linear additivity were due to faulty experimental evidence, and that in both the copper–nickel and the copper–gold systems the law is approximately true.[80] A. E. Van Arkel and J. Basart,[81] however, pointed out that the slight deviations from the law of linear additivity are systematic, and, with the help of very accurate powder photographs, they show that a more exact relationship can be established. The law of linear additivity may be expressed in the form

$$L_M = xL_A + (1 - x)L_B,$$

where L_M, L_A, and L_B are the lattice constants (the length of edge of a unit cell) of the alloy M and the pure metals A and B respectively, and x and $(1 - x)$ are the concentrations of the two components. Van Arkel and Basart substitute the more general relationship

$$L_M{}^n = xL_A{}^n + (1 - x)L_B{}^n,$$

and find that $n = 5$ for the copper–gold alloys.

V. M. Goldschmidt [82] has utilised the above law in order to compile a comparable set of interatomic distances for the metals. In the elementary state, the metals crystallise in many different forms. It is, however, quite unsound to compare the interatomic distances in two metals unless their structures are the same, since the value of the interatomic distance is strongly influenced by the degree of co-ordination (the number of neighbouring atoms). To avoid this difficulty, Goldschmidt compares only those metals which crystallise in the hexagonal close-packed system, or in the cubic close-packed system. In either case, the co-ordination number is 12. When the pure metal does not crystallise in either of these ways, Goldschmidt obtains the data from alloys of a metal possessing the above co-ordination number.

Goldschmidt obtains the value of L_B from investigations made on a metal B with a close-packed structure, and the value of L_M from an alloy of A and B with a close-packed structure. L_A can then be calculated from the equation given above. In the absence of data to the contrary, Goldschmidt puts $n = 1$. He obtains the following set of values, N being the atomic number and r the radius (in Å.U.).

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[79] L. Vegard and H. Dale, *Z. Krist.*, 1928, **67**, 148.

[80] Compare C. S. Smith, *Min. and Met.*, 1928, **9**, 458; **A.**, 1313.

[81] *Z. Krist.*, 1928, **68**, 475.

[82] *Z. physikal. Chem.*, 1928, **133**, 397; **A.**, 820.

Atomic radii for a co-ordination number of 12.

	N.	*r*(12).		*N.*	*r*(12).		*N.*	*r*(12).
Mn	25	1·36	Ru	44	1·322	Os	76	1·336
Fe	26	1·27	Rh	45	1·342	Ir	77	1·352
Co	27	1·257	Pd	46	1·370	Pt	78	1·380
Ni	28	1·244	Ag	47	1·442	Au	79	1·439
Cu	29	1·276	Cd	48	1·521	Hg	80	1·55
Zn	30	1·374	In	49	1·569	Tl	81	1·707
Ga	31	—	Sn	50	1·582	Pb	82	1·747
Ge	32	1·394	Sb	51	1·614	Bi	83	1·82

When the co-ordination number is less than 12, the atomic radius is considerably diminished. The effect may be expressed quantitatively as follows :

[12] ⟶ [8] 3% contraction.
[12] ⟶ [6] 4% ,,
[12] ⟶ [4] 12% ,,

This is comparable with the same effect in ionic compounds. The relation between co-ordination number and interatomic distance in the latter bodies may be expressed in the following way :

CsCl NaCl
[8] ⟶ [6] 3% contraction.
NaCl ZnS (Wurtzite, zinc blende)
[6] ⟶ [4] 5%—7% contraction.

Goldschmidt concludes from this that the binding force in metals may after all be very similar to that in ionic compounds. In this connexion a paper by J. E. Lennard-Jones and H. J. Woods,[83] on the distribution of electrons in a metal, is of considerable interest. Considering a two-dimensional lattice, they obtain the average distribution of electrons, using the Fermi–Dirac statistical mechanics. The structure consists of alternate regions of positive and negative electricity, so that there is some justification for the electron-lattice theory of metallic structure,[84] but the structure is dynamic, not static.

W. Hume-Rothery [85] has applied the electron-lattice theory in an attempt to explain some of the properties of metals. The plasticity of metals is supposed to be due to the difference in size between the positive ions and the negative electrons which build up the lattice.

The study of alloys by *X*-ray methods has shown the difficulty of defining the term " inter-metallic compound " in an entirely satisfactory way. A. Westgren and G. Phragmén [86] have suggested

[83] *Proc. Roy. Soc.*, 1928, [*A*], **120**, 727; **A.**, 1299.
[84] Lindemann, *Phil. Mag.*, 1915, **29**, 127; *A.*, 1915, ii, 47.
[85] *Ibid.*, 1927, **4**, 1017; **A.**, 1928, 111.
[86] *Ibid.*, 1925, **50**, 311; *A.*, 1925, ii, 746.

that "in an ideal inter-metallic compound structurally equivalent atoms are chemically identical." W. Hume-Rothery,[87] however, considers that only those substances which may be supposed to show either electron-sharing or electron-transference should be regarded as chemical compounds. Whichever definition be accepted, there remains the difficulty that, for the most part, no clear distinction can be made between solid solutions and inter-metallic compounds, since most alloys are intermediate in character, and often conflicting results are obtained in the study of these substances. The copper–tin system is an interesting case in point.

The copper–tin alloys have recently been investigated by A. Westgren and G. Phragmén [88] and by J. D. Bernal.[89] The α-phase consists of a solid solution with the copper type of structure (face-centred cubic), and the β-phase appears to be a solid solution of the body-centred cubic type; but the δ-, ε-, and η-phases show some extraordinary features. According to Westgren, the ε-phase is a solid solution with a hexagonal close-packed structure. Bernal * has shown that it is much more complex, and that a possible formula would be $Cu_{50}Sn_{16}$, the space group probably being V_h^{17}. The structure is in fact almost hexagonal close-packed, but the copper and tin atoms are too dissimilar to be arranged at random. The departure from hexagonal symmetry is very difficult to detect, and W. M. Jones and E. J. Evans [90] have also reported this structure to be hexagonal close-packed. According to Westgren and Phragmén, the η phase has a nickel arsenide structure, so that its formula should be CuSn, but Bernal finds that Cu_6Sn_5 is nearer the truth, and considers that the unit cell probably contains 230—250 atoms of tin and 280—300 atoms of copper.

The δ-phase of the copper–tin system is also extraordinarily complex, the unit cell, which is face-centred cubic, containing 416 atoms. The range of homogeneity of this phase is extremely narrow, and chemical analysis shows that the formula is about $Cu_{31}Sn_8$, though symmetry considerations show that it is not possible to divide the 416 atoms in exactly this ratio. The formula $Cu_{31}Sn_8$ receives support from the remarkable fact that it has the same concentration of valency electrons as occurs in the alloys Cu_5Zn_8 [91]

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* It should be noted that Bernal's ϵ is Westgren's η, and *vice versa*.

[87] Lindemann, *Phil. Mag.*, 1928, **5**, 173; **A.**, 222.

[88] *Z. anorg. Chem.*, 1928, **175**, 80; **A.**, 1174.

[89] *Nature*, 1928, **122**, 54; **A.**, 822.

[90] *Phil. Mag.*, 1927, (vii), **4**, 1302; **A.**, 1928, 6.

[91] A. J. Bradley and J. Thewlis, *Proc. Roy. Soc.*, 1926, [*A*], **112**, 678; **A.**, **1926**, 1084.

and Cu_9Al_4,[92] which agrees with Hume-Rothery's hypothesis [93] that the ratio of valency electrons to atoms should be the same in analogous phases of the three systems Cu–Zn, Cu–Al, and Cu–Sn. A. J. Bradley and C. H. Gregory,[94] in an investigation of ternary alloys of copper, zinc, and aluminium, show that this type of structure is still preserved in the ternary alloys, so long as the ratio of valency electrons to atoms is maintained.

Westgren and Phragmén [95] have made a detailed attempt to trace the applicability of the Hume-Rothery relationship to a large number of alloy systems. They conclude that the β-phase (body-centred cubic) occurs in the systems Ag–Mg, Ag–Zn, Ag–Cd, Au–Zn, Au–Cd, Cu–Al, Cu–Sn, and Cu–Zn, usually when the ratio of valency electrons to atoms is approximately 3/2. Phases with a structure like that of γ-brass (Cu_5Zn_8) occur in the systems Ag–Zn, Au–Zn, Ag–Cd, Ag–Hg, Cu–Cd, Cu–Al, and Cu–Sn usually when the ratio of valency electrons to atoms is about 21 to 13. Hexagonal close-packed structures appear in the systems Cu–Zn, Ag–Zn, Au–Zn, Ag–Cd, Au–Cd, Ag–Al, Au–Al, Ag–In, Cu–Sn, Ag–Sn, Cu–Sb, and Ag–Sb usually when the ratio of valency electrons to atoms is about 7/4. There are many exceptions to the valency rule, but it is the first successful attempt to systematise alloy structures, and is therefore of great importance.

The silver–cadmium system [96, 97] fits in very well with the Hume-Rothery rule, each of the phases of the copper–zinc system appearing in the correct order; there is, however, a high-temperature modification of the β-phase, stable above 400° and possessing a hexagonal close-packed structure. The silver–aluminium system [98] is only partially analogous to the copper–zinc system. Instead of a body-centred cubic structure, at a concentration of 3/2 valency electrons per atom one obtains a complex structure, isomorphous with β-manganese, the structure of which has been determined by G. D. Preston.[99] He finds that the unit cell is cubic, the length of the side being 6·29 Å., and contains 20 atoms, in agreement with the results of Westgren and Phragmén.[1] The space group is O^6 or O^7 (enantiomorphous forms), and the structure consists of two groups of structurally equivalent atoms, containing respectively 12 and

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[92] A. J. Bradley, *Phil. Mag.*, 1928, **6**, 878.

[93] W. Hume-Rothery, *J. Inst. Metals*, 1926, **35**, 313.

[94] *Mem. Manchester Phil. Soc.*, 1927–1928, **72**, 91.

[95] *Metallwirtschaft*, June, 1928.

[96] G. Natta and M. Freri, *Atti R. Accad. Lincei*, 1927, **6**, 422, 505; 1928, **7**, 406; **A.**, 1928, 223, 464, 820.

[97] H. Åustrand and A. Westgren, *Z. anorg. Chem.*, 1928, **175**, 90; **A.**, 1175.

[98] A. F. Westgren and A. J. Bradley, *Phil. Mag.*, 1928, **6**, 280; **A.**, 1078.

[99] *Ibid.*, **5**, 1207; **A.**, 820.

[1] *Z. Physik*, 1925, **33**, 777.

8 atoms. The composition of the isomorphous alloy is, however, Ag_3Al, so that it is impossible to divide the silver and aluminium atoms into groups of 12 and 8. Most probably they are distributed at random.

Copper–magnesium alloys[2] are entirely different from copper–zinc alloys. There are two phases, CuMg and $CuMg_2$. J. B. Friauf[3] has completely determined the structure of $CuMg_2$. The elementary cell contains 24 atoms, the arrangement of the atoms being the same as that of the metal atoms in spinel.[4] The phase Cu–Mg is face-centred rhombohedral, with 48 atoms in the unit cell. All the alloys so far described contain a metal of the copper–silver–gold group. It is interesting to note, however, that phases analogous to those of the copper–zinc system occur in the iron–zinc[5] system, but there is no approximation to the Hume-Rothery relationship.

Alloys of iron in general show no resemblance to the alloys of the copper group of metals. A striking feature is their tendency to interstitial replacement, small atoms such as nitrogen or carbon readily finding a place in the interstices of the metal lattice. The formation of this type of alloy is an important factor in the hardening of steel. According to W. L. Fink and E. D. Campbell,[6] when eutectoid and hypoeutectoid steels are drastically quenched, a tetragonal structure is formed, intermediate between a body-centred and a face-centred cubic structure. At high temperatures, the carbon atoms occupy positions between the iron atoms, which are themselves on a face-centred cubic lattice. Apparently, on rapid quenching, the carbon atoms have not time to escape from their positions, and this inhibits the change to the body-centred structure, a metastable structure being formed with the carbon atoms still between the iron atoms.[7]

The action of ammonia on iron gives rise to nitrides[8] in which the nitrogen atoms force their way in between the iron atoms. The first effect of this is to transform the iron lattice to the high-temperature structure (γ-iron, face-centred cubic), the nitrogen atoms again occupying the interstices of the structure. A close examination of the structure[9, 10] shows that the nitrogen atoms occupy definite positions, so that the structure probably corresponds to the formula Fe_4N.

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[2] A. Runqvist, H. Arnfelt, and A. Westgren, *Z. anorg. Chem.*, 1928, **175**, 43; **A.**, 1175. [3] *J. Amer. Chem. Soc.*, 1927, **49**, 3107; **A.**, 1928, 109.

[4] (Sir) W. H. Bragg, *Phil. Mag.*, 1915, **30**, 305.

[5] A. Osawa and Y. Ogawa, *Z. Krist.*, 1928, **68**, 177.

[6] *Trans. A.S.S.T.*, 1926, **9**, 716; **B.**, 1926, 919.

[7] N. Seljakov, J. Kurdjumov, and N. Goodtzov, *Nature*, 1927, **119**, 494; *Z. Physik*, 1927, **45**, 384; **A.**, 1927, 400, 1128.

[8] G. Hägg, *Nature*, 1928, **121**, 826; **A.**, 605.

[9] R. Brill, *Naturwiss*, 1928, **16**, 593; **A.**, 940.

[10] G. Hägg, *Nature*, 1928, **122**, 314; **A.**, 1081.

Another type of alloy with interstitial substitution is obtained when hydrogen is dissolved in metals. The well-known case of the palladium–hydrogen "alloys" has been the subject of a large number of investigations by *X*-rays. According to J. O. Linde and G. Borelius,[11] when palladium is heated in an atmosphere of hydrogen, the gas is absorbed in the interstices of the lattice. Up to a certain concentration of hydrogen, depending on the temperature, the palladium lattice (face-centred cubic) is present, but the lattice steadily expands. With greater concentrations of hydrogen, a sudden increase in lattice constant occurs, apparently corresponding to the formation of the compound Pd_2H. When palladium is made the cathode during the electrolysis of dilute sulphuric acid, it absorbs hydrogen and forms a compound PdH with a still greater lattice constant. Spluttered films of palladium, prepared in the glow discharge of hydrogen, are found to have the structure of the metal with an increased lattice constant,[12] and the same is true of platinum. Nickel, however, forms a hydride of the hexagonal close-packed type. In this respect it is analogous to copper,[13] which forms a hydride, CuH, with a hexagonal close-packed structure.

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[11] *Ann. Physik*, 1927, [iv], **84**, 747; **A.**, 1928, 109.

[12] G. Bredig and R. Allolio, *Z. physikal. Chem.*, 1927, **126**, 41; **A.**, 1927, 502.

[13] H. Müller and A. J. Bradley, *J.*, 1926, 1669; **A.**, 1926, 889.

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.

THE work of the two years (1927–28) under review has been rendered distinctive by the experiments of F. W. Aston on the exact masses of isotopes with a new mass-spectrograph, and by the theoretical work of Sir E. Rutherford on the structure of the nucleus of the radioactive atom, particularly with reference to the origin of the α-particle. These investigations promise to enable advances to be made on a wider front than has for some time been possible. On the chemical side, important work has been done on the elements protoactinium and potassium. The activity in attempts to transmute the heavier elements by simple laboratory apparatus, which at the time of the last Report (1926) was at its height, has now subsided; the hostile critics have won, although all the remarkable results obtained during the active period have not yet been withdrawn. No attempt is made in the following pages to summarise all the important work done during the period. Certain topics of interest to chemists have been selected for description and comment in a fuller manner than heretofore, whilst much excellent work of a more physical nature, such as that on details concerning the α-, β-, and γ-rays, has been omitted.

Mass-spectra, Isotopes, and the Packing Effect.

A great advance has been made in knowledge of the isotopic constitution of elements, the masses of the individual atoms on the scale O = 16, and of the "packing fraction" by F. W. Aston [1] with his new mass-spectrograph. (The packing fraction is the divergence of the atom from the whole-number rule divided by its atomic mass, and its importance lies in its being a measure of the gain or loss of mass per proton when the nuclear packing is changed from that of oxygen to that of the atom under examination.) The new mass-spectrograph has five times the resolving power of the old one—far more than sufficient to separate the mass lines of the heaviest elements. The photographed spectrum is nearly 16 cm. long and includes more than one octave of mass, the dispersion scale for a change of mass of 1% varying from 1·5 mm. at the most deflected end to 3·0 mm. at the least deflected end. The accuracy attained is 1 part in 10,000 parts, which is sufficient to give first-order values of the divergence of the masses from whole numbers. Three methods of measuring the mass ratios are described, including the method of coincidences, which consists in photographing in virtual coincidence the lines due to an unknown mass and a known mass, by applying suitable potentials the ratio of which differs by about 0·5% from the expected ratio. The intervals between the lines obtained in this way are measured with a tilting-plate micrometer and converted into intervals of mass by multiplying by the dispersion constants calculated for the mid-point of each interval. The unit of mass is the neutral oxygen atom O^{16}, and the masses measured are corrected for the mass of the electron. They may therefore be compared directly with those of the atomic-weights table. In Table I are given the results of the measurements, with the addition of those for lithium calculated from J. L. Costa's results.[2] It may be noted that the old distinction between the elements which obeyed the whole-number rule and those, like tin, whose masses were found to be less than an integer by 0·1 or 0·2 unit, has disappeared under more accurate work.

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[1] *Proc. Roy. Soc.*, 1927, [*A*], **115**, 487; **A.**, 1927, 914; *Nature*, 1927, **120**, 956.

TABLE I.

Atom.	Packing fraction × 10^4.	Mass (O = 16).	Atom.	Packing fraction × 10^4.	Mass (O = 16).
H	77·8 ± 1·5	1·00778	Cl^{37}	−5·0 ± 1·5	36·980
He	5·4 ± 1	4·00216	A^{40}	−7·2 ± 1	39·971
Li^6	20·0 ± 3	6·012	As	−8·8 ± 1·5	74·934
Li^7	17·0 ± 3	7·012	Kr^{78}	−9·4 ± 2	77·926
B^{10}	13·5 ± 1·5	10·0135	Br^{79}	−9·0 ± 1·5	78·929
B^{11}	10·0 ± 1·5	11·0110	Kr^{80}	−9·1 ± 2	79·926
C	3·0 ± 1	12·0036	Br^{81}	−8·6 ± 1·5	80·926
N	5·7 ± 2	14·008	Kr^{82}	−8·8 ± 1·5	81·927
O	0·0	16·0000	Kr^{83}	−8·7 ± 1·5	82·927
F	0·0 ± 1	19·0000	Kr^{84}	−8·5 ± 1·5	83·928
Ne^{20}	0·2 ± 1	20·0004	Kr^{86}	−8·2 ± 1·5	85·929
Ne^{22}	(*ca.*) 2·2	22·0048	I	−5·3 ± 2	126·932
P	−5·6 ± 1·5	30·9825	Sn^{120}	−7·3 ± 2	119·912
Cl^{35}	−4·8 ± 1·5	34·983	Xe^{134}	−5·3 ± 2	133·929
A^{36}	−6·6 ± 1·5	35·976	Hg^{200}	+0·8 ± 2	200·016
			Pb^{206}	+0·8 ± 2	206·016

The packing fraction gives entirely new information about the nucleus, for it is a measure of the forces binding the protons and electrons together. High packing fractions indicate looseness of packing and therefore low stability; low packing fractions, the reverse. If packing fractions are plotted against the atomic masses it will be seen that, starting at hydrogen with a large positive packing fraction, the curve drops rapidly, crosses the zero line near mass 20 and sinks to a minimum value of $- 10 \times 10^{-4}$ at about Ni^{58} (as shown by later, provisional experiments), rises again, and recrosses the zero line in the region of mass 200. For light masses of elements of even atomic number the initial drop of the curve is

[2] *Ann. Physique*, 1925, [x], **4**, 425; *A.*, 1925, ii, 1021.

much less marked than for the masses of odd atomic number, the two initial parts of the curve joining at about a mass of 40 or 50. It is thus apparent that the fundamental difference between elements of odd and those of even atomic number, already shown in isotopic constitution, in their relative abundance in nature, and in the behaviour of their nuclei under the disintegrating impact of α-particles, applies also to the looseness of the packing of the two sets of nuclei. There is apparently no periodicity in the values of the packing fraction, and the results obtained are considered to be in harmony with Sir E. Rutherford's[3] view of the structure of the nucleus, namely, that it consists of an inner, uniform, tightly bound structure, outside which is a looser system of neutrons, protons, and electrons, which is the more complex the heavier the element.

The accuracy of the measurements and the consistency of the results among themselves leave no doubt that for simple elements the results obtained are the true atomic weights. (When not determined directly they may be obtained accurately from the plot of packing fraction against atomic mass.) In most cases the agreement between these results and those obtained by the ordinary methods of atomic-weight determination is good. The accepted atomic weights of all the simple elements mentioned in Table I are very close to the values of the atomic-weights table; that for phosphorus, 31·04, is probably a little too high.

In the light of these results, it is interesting to consider the three changes in the accepted values of atomic weights recently adopted by the German Commission.[4] The new value for argon, 39·94, is in excellent agreement with the estimated ratio of A^{36} to A^{40}, *viz.*, 1 : 100, and the exact masses of each. The new value for titanium, 47·90, is 0·07 too low, if titanium should be found to be simple; that for yttrium, 89·93, is exactly right. On the other hand, the atomic weight of cæsium deduced from F. W. Aston's results is 132·93, whereas a redetermination by T. W. Richards and M. Françon[5] confirms the accepted value, *viz.*, 132·81. In this case, as the authors point out, the discrepancy may be due to the existence of a second, lighter, isotope in cæsium of mass (it is presumed) 131. This, however, has not been observed by F. W. Aston,[6] and the possibility of the lighter isotope of an element of odd atomic number being less prevalent in nature than the heavier is unusual. The value for the (common) lead isotope 206, *viz.*, 206·016, is in excellent agreement with the latest determination by T. W. Richards and L. P. Hall [7] for uranium-Ω corrected for the presence of thorium-Ω, 206·02, although here a difficulty may be concealed since uranium-Ω presumably contains 3% of the actinium end-product of atomic weight 207 or 209. The fact that the packing fraction for masses above 200 is positive and increasing is consistent with the fact that the values of the atomic weights of thorium and uranium (which, in the chemical sense, are almost certainly simple) are in excess of whole numbers, but not with the value for radium which is accepted as 226·0. This value, as pointed out some years ago,[8] appears to be at least 0·1 unit too low.

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[3] *Infra*, p. 309.

[4] *Ber.*, 1928, **61**, [*B*], 1; **A.**, 1928, 214.

[5] *J. Amer. Chem. Soc.*, 1928, **50**, 2162; **A.**, 1069.

[6] *Ann. Report*, 1922, **19**, 270.

During the period under review knowledge of the isotopic constitution of seven elements has been extended. The results are given in Table II.

TABLE II.

Element.	Atomic number.	Minimum number of isotopes.	Masses of isotopes in order of intensities.[9]
Neon	10	3	20, 22, 21
Zinc	30	7	64, 66, 68, 67, 65, 70, 69
Germanium	32	8	74, 72, 70, 73, 75, 76, 71, 77
Tin	50	11	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
Xenon	54	9	129, 132, 131, 134, 136, 128, 130, 126, 124
Mercury	80	7	202, 200, 199, 198, 201, 204, 196,
Lead	82	4	208, 206, 207, 209

The results for neon, obtained by T. R. Hogness and H. M. Kvalnes [10] with a mass-spectrograph of the Dempster type, confirm the original (but subsequently doubted) result of F. W. Aston [11] that a small proportion of the isotope 21 exists; this proportion is now found to be about 2% of the whole. The results for zinc were obtained by F. W. Aston [12] with the new mass-spectrograph,[1] using a specimen of zinc methyl; they supplement the earlier results of A. J. Dempster.[13] The remainder of the results given above were obtained with the same instrument. Those for tin, xenon, and mercury are extensions of results previously published, and refer to isotopes present in relatively very small concentrations; the new isotope, 196, of mercury, for example, constitutes only 0·04% of the whole. The results for lead,[14] obtained with a specimen of lead tetramethyl, are new. Indications were also given in lead of small proportions (not necessarily smaller than that of isotope 209) of masses 203, 204, and 205, but these could not be ascribed with certainty to lead owing to the presence of mercury. From a general survey of F. W. Aston's results certain other points stand out clearly. First, isobares, hitherto confined to masses of even number, are now extended to those of odd number; for instance, the mass 75 is common to germanium and to arsenic, 69 to zinc and gallium. Secondly, there appears to be no simple rule to describe either the number or the order of intensities of the isotopes of elements of even atomic number; further investigation tends to reveal isotopes undetected in the initial investigation. Thirdly, elements of odd atomic number seem much less complex; their isotopes seem limited to two, the masses of which (beyond nitrogen) are of odd number and differ by two, and their proportion in nature is often approximately a simple one such as 1 : 0, 1 : 1, 3 : 1, the lighter being not the less prevalent; in consequence, if the atomic weight of an element of odd atomic number be definitely in excess of an integer, the element is probably a mixture of two isotopes.

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[7] *J. Amer. Chem. Soc.*, 1926, **48**, 704; **A.**, 1926, 449.

[8] A. S. Russell, *Nature*, 1924, **114**, 717; *A.*, 1924, ii, 813.

[9] The order of the isotopes of sulphur is given correctly in *Ann. Report*, 1926, **23**, 281, but not subsequently.[1]

[10] *Nature*, 1928, **122**, 441; **A.**, 1169.

[11] *Phil. Mag.*, 1920, [vi], **39**, 454; *A.*, 1920, ii, 277.

[12] *Nature*, 1928, **122**, 345; **A.**, 1069.

[13] *Physical Rev.*, 1922, [ii], **20**, 631; *A.*, 1923, ii, 413.

[14] *Nature*, 1927, **120**, 224; **A.**, 1927, 806.

Separation of Isotopes, and the Radioactivity of Potassium.

During the period under review, negative results have been obtained in several investigations [15] carried out with a view to show that different isotopic concentrations of an element may be obtained from different sources of material. H. V. A. Briscoe, P. L. Robinson, and H. C. Smith,[16] however, continuing their work on boron, find a real difference of approximately 0·01 in the mean atomic weights of boron from California and from Asia Minor. Several attempts [17] to concentrate one isotope in a mixture have also failed. E. R. Jette [18] discusses the available theoretical and experimental work on the possibility of separating isotopes by methods which depend on the assumed influence of the different masses of the isotopic ions on their mobilities in solution, and concludes that none of them can lead to a positive result.

Notable successes have been obtained by W. D. Harkins and B. Mortimer [19] with mercury, and by W. D. Harkins and C. E. Broeker [20] with chlorine. With mercury, their former apparatus has been modified to allow of more rapid working, and mercury with an atomic weight differing by 0·189 unit from that of ordinary mercury has been obtained by fractionation. This is a record difference. With chlorine, a diffusion method with hydrogen chloride left 1/8000th of the original gas, which on analysis had an atomic weight approximately 0·055 unit higher than that of chlorine. The work of G. von Hevesy and co-workers [21] on the concentration of the isotope of mass 41 of potassium is of double importance because it throws light on the feeble radioactivity of this element and by inference on that of rubidium. In order to discover which of the isotopes is responsible for the emission of the β-particles, they submitted one litre of liquid potassium to ideal distillation, the metal being maintained at 160°, and the potassium surface, on which condensation took place, being cooled by solid carbon dioxide; the distance between hot and cold surfaces was maintained at less than 1 cm. The final residual fraction was found to have an atomic weight of 39·109, which is 0·005 unit greater than that of ordinary potassium. It contains therefore, it was calculated at the time, 4·8% more of the isotope of mass 41 than does ordinary potassium. (Recalculated on F. W. Aston's exact values [22] for the isotopes of potassium, this value becomes 4·0%). The activities of equal masses of the chlorides of the heavy residual fraction and of ordinary potassium were compared by means of Hoffman's vacuum electrometer and the difference was found to be 4·2 ± 0·7%. This result agrees so well with that to be expected from the observed change in atomic weight that it is concluded that the isotope 41 is solely or mainly responsible for the β-particles emitted. Interesting deductions are made from this remarkable result. First, if it be assumed that rubidium owes its activity to its higher isotope, its greater activity than that of potassium is simply explained—for there is more of it. Cæsium, on the other hand, having apparently one isotope only, may be said to have no heavier isotope and therefore no radioactivity. (There are objections, however, to this view. It assumes a connexion between the alkali elements and radioactivity which is *a priori* unlikely. Again, it is not impossible, as has been mentioned above, that cæsium has a lighter isotope; if so, the abundant heavier isotope, which actually is inactive, should be active.) Secondly, the value for the half-period of potassium, given by A. Holmes and R. W. Lawson,[23] now requires correction to the value they gave on the assumption that the activity of potassium is due to the mass 41, *viz.*, 7·5 × 10^{10} years, a result of the order of the half-period of thorium. From this period it may be calculated that 2% of this isotope has disintegrated since the consolidation of the earth's crust, and that at one time the atomic weight of terrestrial potassium was as much as 0·002 unit greater than now. If the emission of the β-particle effects an alteration in the nuclear charge, the product of transformation of potassium will be the calcium isotope 41, a product hitherto not detected in nature, but one which should show itself in an atomic-weight determination of calcium extracted from old potassium minerals. Potassium, which expels β- but no α-particles and has an enormous half-period for the isotope which expels β-particles, presents an interesting contrast to a (heavy) radioactive element where the emission of α- is always more obvious than that of β-particles, and where the nuclear β-particle, when detectable, is never associated with a product of half-period greater than 20 years.

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[15] (Mlles.) E. Gleditsch and L. Gleditsch, *J. Chim. physique*, 1927, **24**, 238; **A.**, 1927, 493; K. R. Krishnaswami, *J.*, 1927, 2534; **A.**, 1927, 1120.

[16] *J.*, 1927, 282; **A.**, 1927, 392.

[17] H. S. King, *J. Amer. Chem. Soc.*, 1927, **49**, 1500; **A.**, 1927, 709.

[18] *Phil. Mag.*, 1927, [vii], **3**, 258; **A.**, 1927, 182.

[19] *Ibid.*, 1928, [vii], **6**, 601; **A.**, 1301.

[20] *Z. Physik*, 1928, **50**, 537; **A.**, 1301.

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[21] *Nature*, 1927, **120**, 838; **A.**, 1928, 4; M. Biltz and H. Zeigert, *Physikal. Z.*, 1928, **29**, 197; **A.**, 454; G. von Hevesy and M. Lögstrup, *Z. anorg. Chem.*, 1928, **171**, 1; **A.**, 684.

[22] *Supra*, p. 304.

[23] *Nature*, 1926, **117**, 620; **A.**, 1926, 554; *Phil. Mag.*, 1926, [vii], **2**, 1218; **A.**, 1927, 86.

Structure of the Radioactive Nucleus and Origin of the α-Particles.

Sir E. Rutherford [24] has put forward a singularly complete theory of the structure of the nuclei of radioactive atoms, based on, and discussed in terms of, the experimental data. The two sets of observations on which the theory is largely based are: (1) The fact that in radioactive transformations an α-particle from a given atom is expelled with a remarkably constant speed; this is regarded as a strong indication that the α-particle in the nucleus is circulating in a quantised orbit and released therefrom at a definite characteristic velocity. (2) Although experiments on the scattering of α-particles appear to indicate that the nucleus of a heavy atom such as uranium must have a radius smaller than 3·2 × 10^{-12} cm., computation from radioactive data makes the nuclear radius at least twice as great as this. This divergence is most easily explained by the assumption that if any constituent particles of the nucleus extend to a distance of 6 × 10^{-12} cm. they must be electrically neutral. These neutral particles circulating round the inner nucleus are regarded as being held in equilibrium, either by magnetic forces arising from the inner nucleus, or by attractive forces due to the distortion or polarisation of the particle itself by the electric field. In the theory the latter forces are considered operative, since little is known of the former. First is considered theoretically the motion of a neutral satellite moving in a circular n-quantum orbit around the central nucleus under the attractive forces due to polarisation of their structure by the field from the nuclear charge;

[24] *Phil. Mag.*, 1927, [vii], **4**, 580; **A.**, 1927, 1002.

then the theory is modified to account for the fact that the neutral satellite escapes as a doubly-charged particle. It is supposed that the satellite loses its two electrons and becomes the α-particle when the energy stored in it due to distortion falls below a certain critical value, the same for all α-particles. Various relations are derived, principally one connecting the energy of emission of an α-particle with the fourth power of the quantum number n and three constants. The values of these constants are obtained from the data of the uranium–radium series, and when quantum numbers (in some cases half quantum numbers) are assigned to each product of the three series expelling α-particles, the energies of emission of α-particles calculated from this relation are found in all cases to be in agreement (within the error of experiment) with those determined experimentally; the agreement is particularly striking for the members of the thorium series. Certain quantum orbits are found to be common to two elements; the number 24, for example, is assigned both to radium-*A* and to thorium-*C*, the number 23·5 to both thorium-*X* and actinium-*X*. On this theory, the existence of the long-range α-particles expelled by radium-*C′*, thorium-*C′*, and actinium-*C* receives a ready explanation, *viz.*, that while the majority of the atoms break up in one way due to the liberation of the satellite from a definite quantum orbit, a small proportion of the atoms may liberate satellites from other and presumably deep-seated orbits. Thus the long-range particles from both radium-*C′* and thorium-*C′* correspond with the quantum number 31, whereas the ordinary α-particle from the former product corresponds with the number 28 and that from the latter with the number 30.

In the calculations which lead to this successful issue, the radius of the satellite (which later becomes the α-particle) is found to be about 6×10^{-13} cm., and hence the volume is approximately 1×10^{-36} c.c. This is in good agreement with the volume ($0{\cdot}5 \times 10^{-36}$ c.c.) calculated from the experimental results of J. Chadwick and E. S. Bieler [25] for the region surrounding the particle where the forces are known to be abnormal. Reasons are next given for anticipating that the radioactive constant λ should be connected, not with the final energy of escape of the α-particle, as it is in Geiger and Nuttall's relation, but with the quantum number characterising the orbit which is liberated, and with a quantity depending on the constitution of the central nucleus. The relation found, although satisfactory, is not as simple as was anticipated.

The theory extends also to the γ-ray which is known, from the work of C. D. Ellis, (Frl.) L. Meitner, and others, to have its origin in the nucleus. The γ-ray is considered to arise when a satellite

[25] *Phil. Mag.*, 1921, [vi], **42**, 923; *A.*, 1922, ii, 12.

moves from one quantum level to another, a view in harmony with results for radium, actinium-X, radioactinium, etc., where the γ-ray either accompanies or follows transformations in which only α-particles are emitted. Coincidences are found (within experimental error) between the observed energy of the γ-rays and energy differences between various levels. The agreements are regarded, however, with some diffidence, owing to the large number of energy levels possible, and further discussion is reserved for a later communication.

On this theory the nucleus has three well-defined regions in its structure. The inmost part is very compact with a volume of radius not greater than 1×10^{-12} cm., a closely ordered, "crystalline" arrangement of its component electrons and protons. This central nucleus probably does not vary regularly in charge and mass from atom to atom but is common to several elements; it is quite likely that it is common to all the elements of a radioactive series. Round this central part is a region extending to a radius of about $1{\cdot}5 \times 10^{-12}$ cm., occupied by electrons and possibly also charged nuclei of small mass; the electrons here circulate with velocities close to that of light. Outside is the comparatively large volume between radii of $1{\cdot}5 \times 10^{-12}$ and 6×10^{-12} cm., probably occupied by a number of neutral satellites held in equilibrium by the polarising action of the electric field arising from the central nucleus. No definite information is yet available as to the number of these, or whether they are all of the same kind; radioactive evidence suggests that helium satellites are there, and a study of the relative masses of isotopes by F. W. Aston suggests that masses of 3, 2, and possibly 1 are also present. From the theory it is calculated that helium satellites are possible in the nucleus of an atom of as low an atomic number as 15, and should become numerous for an atomic number of 30—a result which is in agreement with the fact that the average number of isotopes per element increases in a marked manner above element 29. In a radioactive atom one of the neutral helium satellites, circulating in a quantised orbit round the central nucleus, for some reason becomes unstable and escapes, losing its two electrons when the electric field falls below a certain critical value; it leaves the atom with a speed depending on its quantum orbit and nuclear charge. The electrons liberated from the satellite fall towards the central part of the nucleus and circulate with nearly the speed of light in the region between this nucleus and where the satellite had been; if one is hurled out of this system it becomes a disintegration electron. The disturbance to the neutral satellite system by one of the causes mentioned may lead to its rearrangement, involving the transition of one or more satellites from one quantum orbit to another, and this leads to the emission of a γ-ray, the frequency of which is determined by quantum relations.

In this work it was found by the scintillation method that H. Geiger's [26] value for the range of the α-particle from uranium-II is too low, by at least 0·16 cm. This has been confirmed by G. C. Laurence,[27] who measured the range in a Wilson expansion chamber and found 3·28 cm. ± 1%. This alteration in range involves a corresponding change in the estimated value of the product's half-period.[28]

Artificial Transmutation.

The opposition to the claims of transmutation by the use of processes other than swift α-particles, which had begun to set in at the date of the last Report,[29] has now become so strong as to leave little doubt that the claims are quite untrustworthy. F. Bernhardt [30] describes a mercury arc in which quantities of gold of the orders 10^{-7} and 10^{-6} g. have been obtained from mercury originally shown to be free from it, and at one time A. Smits and A. Karssen [31] thought they had obtained as much as 0·1—0·2 mg. of mercury (as iodide) from lead. Other workers, however, announce either completely blank experiments [32] or doubts or withdrawals [33] of their former conclusions. It may therefore be concluded with some certainty that the introduction of an electron into the nucleus by electrical means with consequent formation of one element from another has not been accomplished. B. Walter [34] subjected uranium-X_1 to the action of hard X-rays in the hope that they would eject an electron from the K-ring and that this would be replaced by an electron from the nucleus, and so increase the rate of expulsion of β-particles; the results, however, were negative. H. Herszfinkel and L. Wertenstein [35] attempted to accelerate the rate of radioactive transformation of thorium by bombarding thorium oxide with α-particles from radon but observed no change.

The experiments of F. Paneth and K. Peters,[36] which led to the remarkable conclusion that a minute volume of helium may be synthesised from hydrogen by dissolving the latter in palladium, have now been explained by the authors themselves and P. Günther[37] in a more prosaic but still interesting manner. Helium is not synthesised in detectable amount under the conditions of their experiments: its source is not in the palladium but in the glass. It was found that a glass tube which has been completely freed from its content of helium by heating it in hydrogen takes up a detectable amount of neon-free helium from the atmosphere even after only one day's contact with it. Also, glass tubes which fail to give off detectable quantities of helium when they are heated in a vacuum or in oxygen give off volumes of the order of 10^{-9} c.c. after they have been heated in hydrogen. It is concluded that when an apparatus of glass is used, a trustworthy statement as to the origin of 10^{-9} c.c. of helium cannot be made if air comes in contact with the apparatus, parts of which are later heated in an atmosphere of hydrogen. It may be hoped that the frank withdrawal of an experimental result, which was completely at variance with much of the best-established work on nuclear physics, will encourage those who have arrived at similar sensational results to do likewise. It is abundantly clear, from the experiments which have been described, that in work of this kind, *i.e.*, the formation of one gaseous element from another, the blank experiments have not been sufficiently rigorously carried out. In later experiments the authors[38] have so improved their methods that 10^{-10} c.c. of helium (or neon) can be detected with certainty. With this apparatus they have tested the possibility of the artificial formation of helium from other elements under various conditions, such as bombardment of potassium compounds by cathode rays, passage of an electric discharge, with or without electrodes, through hydrogen or compounds of hydrogen, and the action of β-particles and γ-rays on water and mercury. When precautions were taken to exclude the possibility of the entry of air, or the diffusion of helium from the air through hot glass, or the escape of helium occluded in glass, the results were entirely negative; no quantity of helium larger than 10^{-10} c.c. was obtained.

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[26] *Z. Physik*, 1921, **8**, 45.

[27] *Proc. Nova Scotian Inst. Sci.*, 1927, **17**, 103; **A.**, 1928, 4; *Phil. Mag.*, 1928, [vii], **5**, 1027; **A.**, 684.

[28] *Infra*, p. 319.

[29] *Ann. Report*, 1926, **23**, 286. [30] *Physikal. Z.*, 1926, **27**, 713; **A.**, 1927, 5.

[31] *Z. Elektrochem.*, 1926, **32**, 577; **A.**, 1927, 87.

[32] H. H. Sheldon and R. S. Estey, *Physical Rev.*, 1926, [ii], **27**, 515; **A.**, 1927, 1004; L. Thomassen, *Nature*, 1927, **119**, 813; **A.**, 1927, 606.

[33] A. Smits, *ibid.*, 1927, **120**, 475; **A.**, 1927, 1004; A. Smits and W. A. Frederikse, *Z. Elektrochem.*, 1928, **34**, 350; **A.**, 933.

[34] *Z. Physik*, 1926, **39**, 337; **A.**, 1926, 1190.

[35] *Nature*, 1928, **122**, 504; **A.**, 1169.

[36] *Ber.*, 1926, **59**, [*B*], 2039; **A.**, 1926, 1077.

Preparation and Properties of Protoactinium.

A. von Grosse[39] has for the first time prepared protoactinium (as oxide) in weighable amount by working up large quantities of Joachimstal pitchblende residues. Fusion of the material with potassium carbonate and dissolution of the residues in water removed almost all of the oxides of tantalum and niobium, whereas more than 99% of the protoactinium remained with the insoluble basic oxides; this demonstrates the great difference in basicity between the pentoxides of tantalum and protoactinium. Further concentration showed that protoactinium was remaining quantitatively with the oxides of zirconium and hafnium. The isolation of the first from the other two was effected either by dissolving the oxides in warm dilute hydrochloric acid and precipitating the protoactinium by oxalic acid, or by adding thorium oxide to the mixed oxides and precipitating it as oxalate. In the second case 70—90% of the protoactinium accompanied the thorium in this reaction; the thorium was subsequently removed as fluoride, and the protoactinium finally precipitated from the fluoride by ammonia. By these processes, 2 mg. of protoactinium oxide (probably pentoxide) were obtained in a presumably pure condition, since its activity could not be increased by a repetition of the process of concentration. This material has been used to determine the half-period of the element,[40] and will be used for an atomic-weight determination and for a general study of the chemical and physical properties of the top member of the elements of group VA of the periodic table.[41] The quantity of protoactinium present in uranium minerals is found to be as much as 0·4 g. per g. of radium present.

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[37] *Ber.*, 1927, **60**, [*B*], 808; **A.**, 1927, 429; F. Paneth, *Nature*, 1927, **119**, 706; **A.**, 1927, 606.

[38] *Z. physikal. Chem.*, 1928, **134**, 353; 1928, *B*, **1**, 170; **A.**, 858, 1341.

[39] *Ber.*, 1928, **61**, [*B*], 233; **A.**, 259.

O. Hahn and A. von Grosse [42] have shown that in addition to its principal radiation, the α-particle, protoactinium expels both β-particles and γ-radiation, which are shown to be characteristic and not due to impurity. They find that the absorption coefficient of the β-radiation in aluminium is 126 cm.$^{-1}$. (Frl.) L. Meitner,[43] by photographing the β-particles in a magnetic field, has investigated the γ-radiation emitted, and shown that there are three γ-rays of wave-lengths 0·13, 0·0419, and 0·0382 Å. An interesting deduction is made from a consideration of the β- and γ-radiation emitted by protoactinium and other α-particle elements. It is pointed out that the shortest wave-length of the γ-rays associated with various α-particle changes is of the same order in all cases that have been investigated, whereas with β-ray changes the variations may exceed fifty-fold. Hence it is concluded that the disarrangement of the nucleus produced by expulsion is of the same order for all α-particle emissions but varies widely for different β-particle emissions. For α-particle changes in the same disintegration series, the energy associated with the γ-line of shortest wave-length is greater the longer the half-period of the element emitting it; the inverse is shown by β-particle changes.

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[40] *Infra*, p. 319.

[41] O. Hahn, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1927, 275; **A.**, 1928, 343.

[42] *Z. Physik*, 1928, **48**, 1; **A.**, 569.

[43] *Ibid.*, 1928, **50**, 15; **A.**, 1069.

The atomic weight of protoactinium has yet to be determined directly. Hitherto the general opinion has been that members of the actinium series have atomic weights of the form $4n + 3$ (where n is an integer), the masses of the parent of the series, of protoactinium, of actinium, and of the end-product being 239, 231, 227, and 207, respectively. A. S. Russell[44] has now departed from this view. He shows, from F. W. Aston's results for inactive elements, that the principal isotope of an element of odd atomic number is almost always a mass one unit greater than the principal mass of the element next below it, and, from the results for the uranium and thorium disintegration series, that an isotope which emits a β-particle has a greater mass than one emitting an α-particle. It should, therefore, be expected that 233 is the mass of protoactinium, if this be regarded as the principal isotope of element 91, and that 227 cannot be the mass of actinium, but a number greater than this. On the basis of 233 and 229 for the atomic weights of protoactinium and actinium respectively, those of the head of the series (at. no. 92) and of the end-product (at. no. 82) become 237 and 209, respectively. This value for the uranium isotope is probable in view of F. W. Aston's results for heavy inactive elements, which show that isotopes of masses 1 and 3 less than that of the principal isotope are often found in elements of even atomic number, whilst an isotope of a mass greater by unity is seldom or never found. The view, therefore, that the mass 239 is the head of the actinium series is very unlikely, and, in consequence, the difficulty of explaining why the immediate disintegration products, postulated by this view, have never been discovered does not arise.[41, 45] The principal objection to Russell's view is that it gives for the mass of the end-product of atomic number 82 the value 209, a number which is not only unlikely in itself but is at variance with calculations[46] from atomic-weight determinations of uranium-lead, which lead to values of approximately 207 for the end-product of the actinium series.

Pleochroïc Haloes, the Actinium Series, and "Hibernium."

The interesting suggestion that the actinium series is independent of the uranium series has been made by S. Iimori and J. Yoshimura[47] as the result of an examination of pleochroïc haloes in some specimens of Japanese biotite. Like J. Joly[48] some years ago, they found certain haloes which could not be ascribed to members of the uranium or thorium disintegration series. These haloes possess a common ring of radius 18·2 μ (which is that to be expected from protoactinium), other rings ascribed to members of the actinium series, no ring ascribable to members of the uranium series, but sometimes two very small rings of radii 10·0 and 5·9 μ not unlike the *X*-haloes of Joly (one of which he ascribed to the element "hibernium"). The presence of actinium rings, unmasked by those of members of the uranium–radium series, is regarded as evidence of the independence of the two series. Further, the two small rings are ascribed to isotopes of uranium which precede protoactinium in the series as originally postulated by A. Piccard.[49] As this view is at variance with well-established chemical work, it has been re-examined by A. S. Russell.[50] He agrees with the attribution by the Japanese workers of the outside rings of the haloes to protoactinium and its products, and with their view that the rings of smaller radius are probably identical with the *X*-haloes of Joly, but not with their other conclusions. He ascribes the formation of all abnormal haloes to the alteration of radioactive minerals by agencies such as percolating water. Thus, since protoactinium differs widely in chemical properties from the other elements of a uranium mineral, it has been possibly separated in past time, with or without other products of the disintegration series, from the parent mineral, with the consequent formation of actinium rings unmasked, as normally they are masked, by uranium–radium haloes. In continuation of this argument, the smallest of the Japanese workers' rings is considered to be identical with Joly's hibernium ring, and these are considered to be caused by the feeble radioactivity of the end-product of the thorium series. The other small ring is considered to be identical with another of Joly's *X*-rings, and to be caused by the feeble radioactivity of the end-product of the actinium series. The remaining rings are considered to be due to protoactinium separated with or without lead from either uranium or uranium–thorium minerals. On this view, the disintegration series are partly extended to mercury, and the element hibernium is identified as thorium-Ω. Direct observation of α-particles from the end-products of the thorium and actinium series has, however, not yet been obtained; the activity, if it exists, would be so feeble as to make identification of the particles a matter of great experimental difficulty.

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[44] *Nature*, 1927, **120**, 402; **A.**, 1927, 1002.

[45] E. W. Walling, *Diss.*, *Berlin*, 1928, 43.

[46] F. Lotze, *Z. anorg. Chem.*, 1928, **170**, 213; **A.**, 684.

[47] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1926, **5**, 11; **A.**, 1926, 990.

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[48] *Proc. Roy. Soc.*, 1922, [*A*], **102**, 682.

[49] *Arch. Sci. phys. nat.*, 1917, **44**, 161; *Physikal. Z.*, 1922, **23**, 1.

[50] *Nature*, 1927, **120**, 545; **A.**, 1927, 1003.

Possibility of the Existence of Elements 85 *and* 87.

This question, which has become of added interest to chemists since the discovery of the last of the undiscovered inactive elements, has been discussed by O. Hahn [51] and by G. von Hevesy.[52] A product of atomic number 87 (eka-cæsium) might be produced from one of atomic number 89 emitting an α-particle or from one of atomic number 86 emitting a β-particle. Hahn added a cæsium compound to a strong mesothorium preparation and then removed all known radioelements from it by chemical treatment. If a product of atomic number 87 were there it would remain with the cæsium, and if its half-period were not shorter than 2 hours and if at least 10^{-4} of the atoms of mesothorium-2 emitted α-particles it would not have escaped detection. It was not, however, detected. Similar experiments with actinium were not tried owing to lack of a sufficiently concentrated preparation. G. von Hevesy was unable to detect α-particles from mesothorium-2, the existence of which necessitates a product of atomic number 87, and concludes that less than 1 in 200,000 atoms of mesothorium-2 breaks up in this way. Trials to find a product of atomic number 87 as a β-product of radon by removing chemically all the known members of the active deposit of 100 millicuries also failed. Preliminary experiments to find a product of atomic number 85 as a β-product of the short-living isotopes of element 84 also gave negative results.

It would seem from experiments of this kind that the existence of elements 85 and 87 is going to be very hard to substantiate, and it may be asked whether present knowledge of radioactive processes is favourable or not to the existence of these elements. Can it be said that it is in the highest degree unlikely that these elements will ever be discovered on the earth? All masses of atomic number greater than 83 are known to be radioactive, and, within the limits of atomic number 92—81, those of even atomic number are on the whole more stable than those of atomic number one greater. It may, therefore, be presumed that no product of element 87 would have the period of radon, and no product of element 85 that of polonium. If this be granted, it is certain that elements 85 and 87, created by the same cosmic process that brought into being the other elements, have long ago disappeared. Their only chance of existence lay in their being members of one of the known disintegration series, but it is known that none of these passes directly through atomic number 85 or 87 or, as the experiments mentioned above indicate, indirectly by forming branches. The case against the possibility of existence of these elements appears overwhelming save for one thing. It may be argued that we know nothing of the stability of the elements other than uranium and thorium greater in atomic number than 83, because they have never been examined. Radium, for example, although the most stable isotope of element 88, is merely a disintegration product of the uranium series, and not the element 88 created by the process that created uranium or lead or tin. This element, even if it has the mass 226, would not, except by a coincidence, have the same stability as radium, because such isobaric isotopes as are known in radioactivity differ in stability (*e.g.*, uranium-Z and uranium-X_2; radium-D and radium-Ω'). Hahn believes in the possibility of more stable isotopes of elements 88 and 84, and von Hevesy in that of a stable isotope of element 84. So long as isotopes of elements 88, 86, and 84, more stable than those furnished by the disintegration series, are possible, so long is it possible to argue that some day isotopes of elements 85 and 87 may be discovered. It should be said, however, that none of these more stable isotopes has been discovered; pleochroïc haloes afford no evidence of them, and, in the case of element 86, an exhaustive search made by F. W. Aston,[53] using the methods of positive rays, was without result. It may be concluded that, whilst an investigation with comparatively enormous supplies of known radio-elements may demonstrate the existence of these elements as branches of the main disintegration series, their independent existence in nature is very unlikely. Their rarity is probably so different in degree from that of the other recently discovered elements as almost to be a difference in kind.

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[51] *Naturwiss.*, 1926, **14**, 159.

[52] *Kgl. Danske Videnskab. Selsk. math.-fys. Medd.*, 1926, 7, No. 11, 1; **A., 1927, 289.**

Radioactive Constants and other Data.

The conflict [54] regarding the value of the half-period of radium-E may now be regarded as settled in favour of the higher value; L. F. Curtiss,[55] in a new determination, finds a value of 4·975 days, in good agreement with the results of G. N. Antonov, (Frl.) L. Meitner, and L. Bastings, but not with those of G. Fournier and K. Thaller. M. A. da Silva [56] obtained the value of 140·2 days for the half-period of polonium, in good agreement with the accepted value. A new determination by O. Hahn and O. Erbacher [57] of the half-period of mesothorium-2 gives a value (*viz.*, 6·13 hours) which is 1% less than the original value but 3% greater than that of W. P. Widdowson and A. S. Russell [58] and is probably the most accurate value. From a new relation between the disintegration constant and the quantum number of the element emitting the α-particle, Sir E. Rutherford [59] has deduced that the half-period of uranium-II is less than that of ionium and is about 100,000 years. A smaller value than this (*viz.*, 13,000 years) has been obtained by G. C. Laurence [60] by applying the Geiger–Nuttall relation to his new determination, 3·28 cm., of the range of the α-particles of uranium-II. Both these values are much smaller than the hitherto estimated value of 2,000,000 years. In O. Hahn's laboratory two independent estimates of the half-period of protoactinium have been made: A. von Grosse [61] has obtained a value of 20,000 years from a determination of the amount of pure protoactinium extracted from a known weight of uranium ore, and E. W. Walling [62] arrived at the same result by measuring the rate of growth of protoactinium in uranium originally carefully freed from it. From the result that the radioactivity of potassium is wholly or mainly to be ascribed to its isotope 41, the half-period of this isotope is deduced to be $7{\cdot}5 \times 10^{10}$ years.[63]

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[53] *Proc. Roy. Soc.*, 1923, [*A*], **103**, 462; *A*, 1923, ii, 487.

[54] *Ann. Report*, 1926, **23**, 293.

[55] *Physical Rev.*, 1927, [ii], **30**, 539; **A.**, 1928, 4.

[56] *Compt. rend.*, 1927, **184**, 197; **A.**, 1927, 182.

[57] *Physikal Z.*, 1926, **27**, 531; **A.**, 1926, 990.

The initial velocities of the α-particles from radium-*C*, thorium-*C*, and thorium-*C′* have been determined by G. H. Briggs [64] as $1{\cdot}923 \times 10^9$, $1{\cdot}705 \times 10^9$, and $2{\cdot}053 \times 10^9$ cm./sec. respectively. The first of these determinations is in excellent agreement with the original determination by Sir E. Rutherford and H. Robinson,[65] *viz.*, $1{\cdot}922 \times 10^9$ cm./sec. S. W. Watson and M. C. Henderson [66] have determined the number of α-particles from thorium-$C + C'$ as $(4{\cdot}26 \pm 0{\cdot}08) \times 10^{10}$ per sec. per curie-equivalent of γ-ray activity when in equilibrium with radiothorium and when measured by the γ-rays from thorium-C'' through 1·8 cm. of lead. S. W. Watson [67] has made a new determination of the heats emitted by radon in equilibrium with its products of short life, by radium-$B + C$, radium-*C*, thorium-$B + C$, and by thorium-*C*. The results obtained agree within 1 or 2% with the theoretical values calculated from V. Hess and R. W. Lawson's [68] result for the number of α-particles emitted per sec. by 1 g. of radium, *viz.*, $3{\cdot}72 \times 10^{10}$, and render the lower value of H. Geiger and A. Werner [69] ($3{\cdot}4 \times 10^{10}$) not impossible but unlikely. They are as follows (observed values in g.-cal. per g.-hr. precede calculated values): radon 101·6, 102·4; radium-*B* + *C* 43·1, 43·8; radium-*C* 42·9, 43·4; thorium-*B* + *C* 50·7, 49·7; thorium-*C* 47·9, 47·2. Support for the lower value, however, is afforded by the results of H. Jedrzejowski,[70] who determined the mean value of the total charge of the α-particles emitted in 1 sec. by 1 g. of radium as 33·4 *E.S.U.*; hence the number of α-particles emitted per sec. by 1 g. of radium is $3·50 \times 10^{10}$. (Mlle.) I. Curie and F. Joliot[71] have determined the number of ions produced by a single α-particle from radium-*C′* and find the value $2·2 \times 10^5$, assuming $3·7 \times 10^{10}$ as the number of α-particles emitted per sec. by 1 g. of radium. A. Holmes and R. W. Lawson,[72] after a critical review of the available data, give two formulæ (one approximate and one corrected) for calculating the ages of radioactive minerals from a knowledge of their percentage composition. The approximate formula is: Age (years) = $7·4 \times 10^9$ Pb/(U + 0·38 Th), where Pb, U, and Th denote the % of lead having radioactive origin, of uranium, and of thorium in the mineral. The corrected age is: Approximate age × $(1 - x/2 + x^2/3)$, where $x = 1·155$ Pb/(U + 0·38 Th).

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[58] *Phil. Mag.*, 1925, [vi], **49**, 137; *A.*, 1925, ii, 463.

[59] *Ibid.*, 1927, [vii], **4**, 580; **A.**, 1927, 1002.

[60] *Ibid.*, 1928, [vii], **5**, 1027; **A.**, 684.

[61] *Ber.*, 1928, **61**, [*B*], 233; **A.**, 259.

[62] *Diss., Berlin*, 1928.

[63] *Supra*, p. 309.

[64] *Proc. Roy. Soc.*, 1928, [*A*], **118**, 549; **A.**, 569.

[65] *A.*, 1914, ii, 789.

[66] *Proc. Camb. Phil. Soc.*, 1928, **24**, 133; **A.**, 214.

[67] *Proc. Roy. Soc.*, 1928, [*A*], **118**, 318; **A.**, 455.

[68] *Phil. Mag.*, 1924, [vi], **48**, 200; *A.*, 1924, ii, 649.

[69] *Z. Physik*, 1924, **21**, 187; *A.*, 1924, ii, 226.

Radioactivity and Solar Radiation.

The remarkable observations by (Mlle.) S. Maracineanu described and commented on in the last Report[73] have been continued.[74] Lead, zinc, and copper after exposure to the sun, and lead after being subjected to positive and negative voltages of 120,000, were found to acquire a radioactivity which cannot be explained as due to emanation or active deposit in the atmosphere. It is concluded that lead, insolated for a sufficiently long period, produces a new radioactive substance which emits α-particles and is not unlike polonium in its half-period. It is suggested that under the influence of the sun polonium and even radium-*D* are integrated from the lead. These experiments have yet to be repeated by other observers, and until this is done and the results are confirmed it is probably wiser to ascribe them to less interesting but more natural causes: to an effect of the sun on the surface of the lead so that radioactive impurities therein have their radiations temporarily less strongly absorbed, to the presence of radioactive substances in the atmosphere, and to the daily variation of the natural leak of the measuring instrument. The observations are not unlike those of "induced activity" which were common in the literature about 27 years ago. The fact that the effects have been observed with zinc and copper, as well as with lead, may be taken as conclusive evidence that they are not due to any fundamental action of the sun's rays on the atoms they strike. On modern views of the structure of the atom it seems impossible that solar radiation could produce polonium from lead.

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[70] *Compt. rend.*, 1927, **184**, 1551; **A.**, 1927, 710; *Ann. Physique*, 1928, [x], 9, 128; **A.**, 343.

[71] *Compt. rend.*, 1928, **187**, 43; **A.**, 810.

[72] *Nature*, 1926, **118**, 478; **A.**, 1926, 1075.

[73] *Ann. Report*, 1926, **23**, 294.

[74] *Compt. rend.*, 1927, **184**, 1322, 1547; **185**, 122; 1928, **186**, 746; **A.**, 1927, 605, 710, 807; 1928, 455.

Cosmic Rays and Stellar Matter.

Work on the penetrating extra-terrestrial radiation has been continued [75] by R. A. Millikan and G. H. Cameron [76] and, although necessarily speculative, results of great interest have been obtained. Experiments with pilot balloons show that it is unlikely that there are radiations intermediate in wave-length between γ-rays and the cosmic rays. Definite bands in the cosmic-ray spectrum are found, and these are produced, it is suggested, by definite and continually recurring atomic transformations which involve energy changes altogether of a much greater magnitude than those which occur in radioactive processes; they are not likely to be caused, therefore, by such processes. Their most likely source is the building up of helium from hydrogen, of oxygen from hydrogen, and of silicon from hydrogen or from helium. The calculated absorption coefficients per metre of water of the rays produced by the first three of these processes are, respectively, 0·30, 0·075, and 0·043, and there is experimental evidence that the cosmic rays include radiations having absorption coefficients per metre of water of 0·35, 0·08, and 0·04. From the close similarity of these sets of values, it is concluded that there is continuous creation of helium, oxygen, and silicon in the universe out of protons and electrons. In a later paper [77] further points are discussed. As to the place of origin of the cosmic rays, it is concluded from kinetic and other evidence that the nuclear combinations which produce them do not take place in the stars, as has hitherto been imagined, but at places of low pressure where the temperature is not far from the absolute zero: in interstellar or intergalactic space. There the radiation from the stars is converted, under the conditions of zero temperature and zero density, into protons and electrons, and there the common elements are built up. This bold assumption appears to remove many difficulties. Gone is the difficulty of explaining why the protons and electrons which produce the cosmic rays have not long ago been used up; nor is there now need to suppose, as has been done, that the process of conversion of mass into radiant energy is either nowhere reversible or everywhere reversible. With the stars in one place and interstellar space in another, each functioning appropriately, one's loss is the other's gain, and the universe may be regarded as being now and forever in a steady state. Such revolutionary views are not likely to obtain universal acceptance from physicists and astronomers, and critical discussion of them has begun.[78]

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[75] *Ann. Report*, 1926, **23**, 294.

[76] *Proc. Nat. Acad. Sci.*, 1928, **14**, 445; **A.**, 811.

[77] *Physical Rev.* 1928, [ii], **32**, 533; **A.**, 1303.

A. S. RUSSELL.

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[78] Sir E. Rutherford, *Proc. Roy. Soc.*, 1929, [*A*], **122**, 1.

CATALYSIS.

In accordance with the tendency exhibited in Annual Reports of recent years, we have attempted rather to survey the literature in particular fields germane to the subject of Catalysis than to attempt to prepare a complete abstract of all the varied communications made on the subject during the period under review.

Low-temperature Oxidation.

Catalysts and Inhibitors.—The study of low-temperature oxidation, autoxidation, and antioxygenic action has received much attention during recent years. Two valuable summarising papers have recently appeared.[1, 2]

Attention was called at the General Discussion of the Faraday Society on Homogeneous Catalysis to a number of points in connexion with these phenomena and their explanation as chain reactions. As a result of the very large number of experiments on low-temperature oxidation and inhibition C. Moureu and C. Dufraisse[1] have shown that substances may possess both pro-oxygenic and antioxygenic activity, though the former is not generally very intense, and they differentiate between these substances—iodine, for example, with styrene—and those substances which, although as a rule practically inert towards oxygen, are oxidised in the presence of a catalyst which is itself first oxidised, as, for example, the oxidation of dextrose in the presence of cerium salts (Job, 1900). In many cases a catalyst may have either one function or the other in the same or different reactions.

The question at once arises as to whether the action of anti-oxygens may not be due to their destruction of positive catalysts, which are almost certainly present. The apparent necessity for traces of water in certain reactions would support the necessity of some such catalyst. According to Moureu and Dufraisse, Titov showed that the inhibitory action of benzyl alcohol, etc., on the oxidation of dilute sulphite solutions acted in this way, and other examples may be cited. Where the reaction proceeds on the walls or on a surface, there can be no doubt that an inhibitor can poison the necessary active areas and thereby stop the reaction, as was shown by M. Brunner,[3] O. M. Reiff,[4] and E. K. Rideal and (Miss) W. M. Wright.[5] The extraordinary efficiency of small traces of positive catalysts can be noticed in the experiments of R. Kuhn and K. Meyer,[6] who have shown that very carefully fractionated benzaldehyde, in a carbon dioxide atmosphere, can, when the greatest precautions are taken, be made inert to oxygen. The action is immediately induced by the presence of exceedingly small amounts of heavy metals, iron, copper, nickel, and manganese salts all being effective, the iron being 15 times more active in the ferrous condition than in the ferric; inhibition by phenol is prevented by iron salts. It seems impossible to account fully for all the facts on this hypothesis. Moureu and Dufraisse, with many other authors, believe that the first step involves the union of one molecule of oxygen with one of the autoxidisable substance to form the primary peroxide, $A[O_2]$, and that energy is absorbed in this process, so that only active molecules can undergo the change. The primary peroxide will then possess a very high energy, sufficient to oxidise the antioxygen B. Their scheme for antioxygenic action is then

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[1] *J. Soc. Chem. Ind.*, 1928, **47**, 819, 848.

[2] H. L. J. Bäckström, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, 16; **A.**, 1927, 1151.

$$\begin{aligned} A + O_2 &\longrightarrow A[O_2] \\ A[O_2] + B &\longrightarrow A[O] + B[O] \\ A[O] + B[O] &\longrightarrow A + B + O_2, \end{aligned}$$

or a similar stage involving the direct oxidation of B to B[O] and its subsequent decomposition. The action of the negative catalyst is therefore a positive one in the direction of the reverse reaction.

These schemes are worked out very fully and explain the close relationship between positive and negative catalysts and the easy change from the one to the other. This rise in potential of the active molecules which may then be lost either to the initial state or to the stable state of oxidation has been shown by these authors to be thermodynamically sound,[7] and they have applied their results to the preservation of rubber and other easily oxidisable substances.

In the papers quoted above, the objections raised by F. Perrin[8] have been discussed. Perrin's views, based principally on fluorescence effects, are briefly that the deactivation of an excited molecule is due to a free electron, such as might be found in an easily oxidisable substance such as an antioxygen. A chain theory similar to Bodenstein's is regarded as the most probable mechanism; the reacting molecule is supposed to have sufficient energy to cause other molecules to react, and the diminution of the mean lives of the reacting molecules by the inactivating molecules lessens the chance of reaction of the former. Thus antioxygens may inhibit photochemical reactions which are not necessarily oxidations. The question of the reaction chain will be dealt with in greater detail later. Moureu and Dufraisse believe that these catalysts behave as antioxygens and antiluminants on account of two separate influences, and a theory which connects up the two effects cannot be reconciled with the inversion of catalysis in an autoxidation, and the relationship of inverse catalysts. The work of H. Gaffron [9] is explicable by assuming the formation of a primary peroxide, containing active oxygen only, followed by its catalytic destruction with the liberation of oxygen.

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[3] *Helv. Chim. Acta*, 1927, **10**, 707; **A.**, 1927, 1152.

[4] *J. Amer. Chem. Soc.*, 1926, **48**, 2893; **A.**, 1928, 57.

[5] *J.*, 1927, 2323; and earlier papers.

[6] *Naturwiss.*, 1928, **18**, 1028.

[7] C. Moureu and C. Dufraisse, *Compt. rend.*, 1927, **185**, 1545; 1928, **186**, 196; **A.**, 251.

[8] *Compt. rend.*, 1927, **184**, 1121; **A.**, 1927, 609. (See also J. Perrin, *ibid.*, 1928, **187**, 913, on the relations of light in a thermal chemical reaction.)

In two recent papers [10] Moureu, Dufraisse, and M. Badoche have examined the inhibition by phosphorus and its compounds; 1% of this element can inhibit the autoxidation of furfuraldehyde whilst increasing that of benzaldehyde, styrene, or turpentine. Red phosphorus may also act, although less strongly, in either direction. Investigations have also been made on phosphorus trichloride, tribromide, oxychloride, and oxybromide, and on hypophosphorous, phosphorous, and phosphoric acids; and the results support the view that an oxygenating catalyst must be able to undergo further oxidation. Moureu, Dufraisse, and J. R. Johnson [11] have published a series of papers on the autoxidation of furylethylene and have examined the effects of numerous inhibiting agents. With G. Berchet,[12] these authors have also studied the autoxidation and polymerisation of chloral, and the effect of small quantities of impurities. The low-temperature oxidation in the presence of oxygen is autocatalytic, depending on the initial formation of a catalyst in the light, after which the reaction can proceed in the dark. Substances such as phenols, etc., and antioxygenic catalysts in general also inhibit the spontaneous polymerisation to metachloral. Moureu, Dufraisse, and Badoche [13] have examined the inhibiting effect of arsenic and its compounds on autoxidation. Arsenic compounds may be positive or negative catalysts.

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[9] *Biochem. Z.*, 1926, **179**, 157; **A.**, 1927, 1225.

[10] *Compt. rend.*, 1928, **186**, 1673; 1928, **187**, 157; **A.**, 849, 967.

[11] *Bull. Soc. chim.*, 1928, [iv], **43**, 586; **A.**, 718.

[12] *Ibid.*, p. 942; **A.**, 1196.

[13] *Compt. rend.*, 1928, **187**, 918.

Intermediate Compounds.

Van der Beek [14] has published two papers on the autoxidation of benzaldehyde in the presence of various catalysts, describing attempts to isolate the intermediate product, perbenzoic acid. As much as 43% of this acid was isolated from an acetone solution after exposure to sunlight and oxygen, and the reaction in benzene solution is believed to be

$$\mathrm{Ph{\cdot}CHO} \longrightarrow \mathrm{Ph{\cdot}CO_3H},$$
$$\mathrm{Ph{\cdot}CO_3{\cdot}H} + \mathrm{Ph{\cdot}CHO} \longrightarrow \mathrm{2Ph{\cdot}CO_2H},$$

but this mechanism cannot obtain in carbon tetrachloride solution. The intermediate products in presence of acetic anhydride were also examined.

H. N. Stephens [15] has similarly isolated the peroxide formed in the low-temperature oxidation of *cyclo*hexene: the product was apparently a dimeric form of the peroxide containing one peroxide group, and about 0·75% was formed in four months.

In continuation of his researches, Wieland [16] has examined the enzyme which causes the autoxidation of quinol, and also the peroxidase obtainable from horse-radish; and H. Wieland and W. Franke [17] have made a very complete study of the activation of oxygen by ferrous salts in solutions.

The induction period of the autoxidation of *n*-hexane has been shown by M. Brunner and E. K. Rideal [18] to be similar to that of benzaldehyde, and is due to the formation of a peroxide which must reach a certain concentration before the rapid oxidation, believed to be due to a chain mechanism, is started. The relation of the temperature and the oxygen pressure to this period was examined, and also the surface combustion on pumice whereby polymerisation products from the decomposition of the peroxide molecules are believed to be formed. More recently, these authors [19] and Brunner alone [20] have examined the reaction in greater detail by freezing out the reaction mixture at stated intervals and examining the products. The induction period is shown definitely to be accompanied by a rapid rise in peroxide or moloxide concentration, which attains a maximum at the same time as the rapid oxidation begins, as measured by the pressure decrease of oxygen. That some slow reaction is also taking place during the induction period was shown by the increasing concentration of carbon monoxide and carbon dioxide and at the same time the fatty acid concentration rises to a steady value which is reached at the same time as the rapid reaction begins. The amount of water formed rises continuously during the first part of the reaction, while the oxygen pressure is falling rapidly. The general reaction schemes proposed by Brunner are the primary reaction

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[14] *Rec. trav. chim.*, 1928, **47**, 286, 301.

[15] *J. Amer. Chem. Soc.*, 1928, **50**, 568; **A.**, 401.

[16] H. Wieland and H. Sutter, *Ber.*, 1928, **61**, [*B*], 1060; **A.**, 921.

[17] *Annalen*, 1928, **464**, 101; **A.**, 965.

[18] *J.*, 1928, 1162; **A.**, 731.

[19] *J.*, 1928, 2824; **A.**, 1350.

[20] *Helv. Chim. Acta*, 1928, **11**, 56.

$$2C_6H_{14} + O_2 \longrightarrow 2C_6H_{12} + 2H_2O,$$

and the moloxide decomposition

$$(C_6H_{14})_2(O_2) \longrightarrow 2C_6H_{12} + 2H_2O$$
$$(C_6H_{14})(O_2) \longrightarrow C_5H_{11}{\cdot}CHO + H_2O$$

whilst the peroxide may react

$$C_5H_{11}{\cdot}CH_2{\cdot}O{\cdot}OH \longrightarrow C_5H_{11}{\cdot}CHO + H_2O,$$
$$C_5H_{11}{\cdot}CH_2{\cdot}O{\cdot}OH + \underset{\text{(acceptor)}}{C_6H_{14}} \longrightarrow 2C_6H_{12} + 2H_2O.$$

The presence of small amounts of oxides of carbon and the general complexity of the reaction, together with the concealed rapid reaction in the "induction period," point to this reaction being much more complex than was originally supposed, and show that direct pressure readings of the total pressure may give completely misleading results. F. Oberhauser and W. Hensinger[21] have noted the production of an activated form of oxalic acid with potassium permanganate, which had the character of an unstable peroxide but was not isolable. Several reactions hitherto regarded as purely homogeneous have been shown to be complex; thus some mutarotations are now known to be sensitive to the presence of the walls of the apparatus, the most recent case being that of tetra-acetyl glucose in ethyl acetate.[22] By use of a very fine technique for the production of clean solutions and surfaces, complete arrest of the mutarotation was possible, and there was evidence that with an alkaline catalyst the reaction might be due to the contaminated surface of the vessel, and the progressive acceleration to some sort of chain mechanism spreading from the surface through the reagents.

K. C. Bailey[23] has examined a similar case, namely, the inhibition by pyridine of the esterification of ethyl alcohol and acetic acid; the reaction is found to occur partly on the walls and partly in the bulk phase, and inhibition may be due to the normal poisoning of the active centres.

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[21] *Ber.*, 1928, **61**, [*B*], 521; **A.**, 505.

[22] T. M. Lowry and G. G. Owen, *Proc. Roy. Soc.*, 1928, [*A*], **119**, 505; **A.**, 967.

[23] *J.*, **1928**, **1204**; **A.**, 718.

E. Puxeddu[24] has discussed the previous work on induction in aqueous solutions, and concludes that these phenomena can all be explained only by postulating an initial period of retardation in all chemical reactions, which in ordinary circumstances is very short. The induction period of the precipitation of sulphates of alkaline-earth metals and of sulphur from thiosulphate by sulphuric acid is shown to be shortened by a rise of temperature or an increase in concentration.

In his studies of silver-ion catalysis, C. V. King[25] has also shown, *inter alia,* that the oxidation of the persulphate ion is strongly catalysed, and that duplication of the results is very difficult, owing to some catalytic effect of the walls: it would appear that this factor in homogeneous liquid reaction may be more common than is generally recognised. H. Moureu[26] has also called attention to the catalytic action of the glass in a study of the isomerism of certain α-diketones, in particular methylbenzylglyoxal and phenylbenzylglyoxal, for which he shows the isomerism to be particularly marked, with a tautomerism greatly affected by catalysts.

(Miss) W. M. Wright and E. K. Rideal[27] have made quantitative studies of the decomposition of hydrogen peroxide on various surfaces, including glass, showing that the rates of decomposition attain a maximum when the electrometric potentials of the surfaces are brought to zero, thus permitting of a maximum absorption of the peroxide. B. H. Williams[28] has also studied the same reaction in glass, silica, and waxed vessels, and has shown the decomposition to be due to adsorbed molecules on the walls or on dust, and particularly on preformed active points on both glass and silica.

Chain Reactions.

Christiansen, in a note communicated to the Faraday Society discussion,[29] has criticised the general theory of Moureu and Dufraisse on the action of inhibitors and oxidation on the main grounds that all their experimental facts are not explicable on this basis. By an analysis of their mechanism, and by examining the velocity coefficients of both the forward and the reverse reaction, he has shown that on their mechanism the addition of B, the inhibitor, could never decrease the velocity of the reaction. That, with the addition of a chain mechanism, their results are readily explicable is well known, and, in particular, H. L. J. Bäckström,[30] who has made some very exhaustive studies on autoxidation, inhibition, and the effect of light on these phenomena, has shown that reaction chains here are necessary. In his earlier papers a very complete account is given of the formation of the reaction chains. He adopts Christiansen's " hot molecule " hypothesis for the production of thermal chains and shows that chains excited photochemically have substantially the same properties. Quantum-efficiency measurements of the length of the chain were made and shown to give a quantum yield of the order of 10,000 to 50,000 mols. per quantum for the photochemical autoxidation of certain aldehydes. This necessarily implies that, when benzaldehyde and the per-acid react under the influence of light, other aldehyde molecules are activated, and the inference is drawn that the thermal reaction proceeds in the same way.

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[24] *Gazzetta,* 1928, **58**, 95; **A.**, 484.

[25] *J. Amer. Chem. Soc.*, 1928, **50**, 2080; **A.**, 964; and earlier papers.

[26] *Trans. Faraday Soc.*, 1928, **24**, 562; **A.**, 1334.

[27] *Ibid.*, p. 530; **A.**, 1196; Wright, *ibid.*, p. 539; **A.**, 1196.

[28] *Ibid.*, p. 245; **A.**, 598.

[29] J. A. Christiansen, *ibid.*, p. 714.

The autoxidation of sulphite solution is similarly studied, and it is shown that all the effects can be accounted for by assuming a chain reaction occurring in two stages. A very complete discussion is given in the papers cited above. Of particular interest is his discussion of the relationship of chemiluminescence and autoxidation, of which a complete bibliography is given, and the conclusions reached are that, as believed by Christiansen, a newly formed reaction product molecule has the energy of the heat of reaction together with the energy of activation, and on collision with another molecule, if they are both rigid, the energy will be dissipated in the form of heat or kinetic energy; but there is also the possibility that the collision may result in the excitation of one molecule (or even more in the case of autocatalytic reactions) to a higher quantum level, which with appropriate restrictions may revert to the normal level with the emission of light. The results of H. Beutler, S. von Bogdandy, and M. Pólányi[31] (see also p. 333) are shown to be in agreement with this. Further, this must lead to photochemical reactions, and the particular case of the decomposition of ozone is examined in detail.

The autoxidation of benzaldehyde, heptaldehyde, and sodium sulphite, which Bäckström himself had studied, are shown to give support to this idea, and photo-sensitisers for these reactions are also investigated. Bäckström criticises Moureu and Dufraisse's scheme[32] for the autoxidation of acraldehyde, and considers that the facts are better explained on a chain hypothesis, with photochemical side chains. In dealing with the action of inhibitors, he shows that, as pointed out by Schönbein, by Moureu and Dufraisse, and by Dhar, an inhibitor of an autoxidation must in general have the properties of an easily oxidisable substance, and his view is that the inhibitor acts by reacting with the per-acid and reducing the number of chains started. It is not completely established that inhibitory power is due to oxidisability, and in the cases where this is not so, the inhibiting agent is stated to act by removing activated molecules of, say, aldehyde, and thus breaking the photochemical chain. The work of F. Perrin (*loc. cit.*) may be cited for comparison.

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[30] *J. Amer. Chem. Soc.*, 1927, **49**, 714; **A.**, 1927, 737; *Medd. K. Vetenskaps-akad. Nobel-Inst.*, 1927, **6**, Nos. 15, 16; **A.**, 1151; *Trans. Faraday Soc.*, 1928, **24**, 601; **A.**, 1335.

[31] *Naturwiss.*, 1926, **14**, 164.

[32] Moureu and Dufraisse, *Compt. rend.*, 1922, **174**, 258; *A.*, 1922, i, 250; *Bull. Soc. chim.*, 1922, **31**, 1152; *A.*, 1923, i, 91; Moureu, Dufraisse, and Badoche, *ibid.*, 1924, **35**, 1591, 1564, 1572; *A.*, 1925, i, 362, 363.

In his most recent paper, Bäckström[33] has confirmed his view of the relationship between inhibition and the induced reaction. Using *iso*propyl, *sec.*-butyl, and benzyl alcohols as inhibitors, he examined the oxidation of sulphites, and by means of colour tests detected the presence of small amounts of acetone, methyl ethyl ketone, and benzaldehyde, as he expected.

A very interesting result of this investigation was that the thermal and photochemical chains had sensibly the same length of about 60 molecules. The inhibitory effect is expressed as the sum of two factors—the breaking of the chains and some other factor—and a quantitative expression is obtained.

N. R. Dhar,[34] in a summary of negative catalysis in slow reaction, has restated his position and added more work. The hypothesis of ion formation will be treated later in greater detail (see p. 343), and he considers that the high quantum yields obtained by Bäckström can be satisfactorily explained by the generation of ions without postulating any chain mechanism. In the thermal oxidation reactions, the negative catalyst acts by actually taking up oxygen and being oxidised, and consequently the two reducing agents compete for the oxygen.

The present position of the theory of chain reactions has been fully dealt with by Christiansen.[35] He emphasises the fact that where a small amount of substance has a great effect on the reaction, that reaction must be complex, so that one of the intermediate products is to a relatively great extent removed by the foreign substance. The possible velocity equations are generalised, and shown to have wide applications.

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[33] *Trans. Faraday Soc.*, 1928, **24**, 601; **A.**, 1335.

[34] *Ibid.*, pp. 565, 567; **A.**, 1335.

[35] *Ibid.*, p. 596; **A.**, 1335.

Low-temperature Flames.

The slow oxidation of phosphorus and the accompanying glow have received a great deal of attention, particularly in the light of the very interesting work of N. Semenoff.[36] It is well known that yellow phosphorus glows in air, but not in oxygen unless the pressure is reduced below a certain value; it has also been shown that there is a lower limit of pressure below which the reaction will not proceed. The glow has been examined spectroscopically,[37] and the reaction is found to be sensitive to the light it emits. In a solution in carbon tetrachloride, Bäckström found a chain length of about 30 molecules per quantum. The presence of ozone is also well known, and this points to the existence of excited molecules of oxygen as well as of phosphorus. The work of (Lord) Rayleigh[38] on the effect of moisture in extinguishing the glow led him to attribute the effect to the failure of the process causing propagation. The presence of ions in this reaction is stated by Busse[39] to be entirely secondary, and he showed that only 1 ion was formed in 8,000,000 reacting molecules; he also found ions in some cases carrying 8 negative charges.

J. Zawidski[40] has developed equations from Russell's[41] values for the velocity of reaction between white phosphorus and oxygen of various degrees of dryness and of various nitrogen contents. J. Chariton and Z. Walta[42] studied the effect of inert gases and of change of pressure, and observed the critical minimum pressure. They suggest that the reacting molecule is P_2, which on reaction liberates heat, thus producing more P_2 from P_4 molecules; this, together with the loss of energy by radiation, prevents the very rapid propagation. M. Bodenstein[43] criticised both the technique and the conclusions, but the criticisms have been met by Semenoff,[36] who considers that Bodenstein's deductions are incorrect. If it is regarded as established that a critical pressure exists below which reaction is very slow, and which depends on the partial pressures of the phosphorus vapour and of the admixed inert gas (*e.g.*, argon), on the diameter of the reaction vessel, and on the temperature, Semenoff shows how the results may be interpreted best on his original branched-chain idea, the chain being broken on the walls. It is assumed that the reaction $P_4 \longrightarrow P_2$ is not instantaneous, that the reacting molecules are activated and may lose energy by collision with the walls, and that the reaction is a chain proceeding very slowly on account of the small number of active centres. It would become explosive in the conditions calculated by Christiansen and Kramers.

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[36] *Z. Physik*, 1927, **46**, 109; **A.**, 1928, 483.

[37] H. Zocher and H. Kautsky, *Trans. Faraday Soc.*, 1926, **21**, 591; H. J. Emeléus, *J.*, 1925, **127**, 1362; *A.*, 1925, ii, 740.

[38] *Proc. Roy. Soc.*, 1923, [*A*], **104**, 322; *A.*, 1923, ii, 755.

[39] *Ann. Physik*, 1927, **82**, 873; **83**, 80; **A.**, 1927, 633, 708.

[40] *Z. physikal. Chem.*, 1927, **130**, 109; **A.**, 1927, 1149.

[41] *J.*, 1903, **83**, 1203.

[42] *Z. Physik*, 1926, **39**, 547; **A.**, 1927, 122.

[43] *Ibid.*, 1927, **41**, 548; **A.**, 1927, 326.

In a very recent paper, Semenoff [44] has studied the oxidation of sulphur vapour, which he finds to behave in sensibly the same manner as phosphorus. Since the induction period is removed by the addition of ozone, he suggests that the active centres are probably oxygen atoms.

This would seem an appropriate place to mention the very interesting work of Hinshelwood and Bogdandy and Pólányi. C. N. Hinshelwood and H. W. Thompson [45] have examined the reaction between hydrogen and oxygen over wide limits, from the heterogeneous wall reaction to the explosion point. Up to 500°, the results are seen to agree with those of Bone and Wheeler,[46] the reaction being accelerated by powdered silica and retarded by steam. From 520° to 530° a reaction of approximately the fourth order, but which varies with the conditions and is strongly autocatalysed by steam, becomes important, and in this reaction the walls have an inhibiting effect. The reaction is accelerated by the addition of nitrogen, or of an inert gas [47] which would lengthen the chain, and this higher-temperature reaction is considered to be a truly gaseous reaction. These authors have no doubt in this reaction as to the reality of the chains, which are lengthened by the elastic collision with the inert gas, or are broken at the walls as in the high-temperature reaction. The latter effect, it is suggested, might be due to the destruction of an autocatalyst for the principal reaction.

A most interesting further study has been made of the results of adding traces of nitrogen peroxide to the reaction mixture. H. B. Dixon observed that a trace of this gas lowered the ignition temperature of hydrogen in air by some 200°. C. H. Gibson and C. N. Hinshelwood,[48] in studying the reaction, observed a slow catalysis which was explicable on the alternate oxidation and reduction of nitrogen peroxide, but at about 400° (or some 200° below the explosion temperature) a definite amount of the gas will cause explosion, and there is a definite lower limit for the amount. At this temperature the normal wall reaction is very slow and if a larger amount of nitrogen peroxide is admitted an equally definite upper limit is reached beyond which only this slow wall reaction takes place. That this is not a catalysed reaction in the ordinary sense is shown by these two sharp limits. These two limits are shown to converge and should meet at about 350°, where there should be only one concentration which would cause the explosion, and experiments made to test this supported the view to some extent.

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[44] N. Semenoff and G. Rjabinin, *Z. physikal. Chem.*, 1928, [*B*], **1**, 192; **A.**, 1332.

[45] *Proc. Roy. Soc.*, 1928, [*A*], **118**, 170; **A.**, 483.

[46] *Phil. Trans.*, 1906, [*A*], **206**, 1.

[47] C. H. Gibson and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1928, [*A*], **119**, 591; **A.**, 960.

[48] *Trans. Faraday Soc.*, 1928, **24**, 559; **A.**, 1334.

This strong effect of a relatively small trace of a foreign substance is believed to be purely a homogeneous one. The nitrogen peroxide may cause the reaction to proceed much faster and behave as a sort of detonator, for if sufficient heat is produced in a volume element of the gas, explosion will result. The upper limit may be due to a falling-off of this detonator reaction or to a dissipation of the heat produced by the nitrogen peroxide itself. Gibson and Hinshelwood make the point that, since the reaction at 530—580° in the absence of the peroxide is quite rapid, it will proceed without a catalyst; and by analogy, the thermal decomposition of ammonium chloride may proceed in the absence of water, which behaves in the same way. This is not evidence for the existence of uncatalysed reactions, but is nevertheless a strong point. H. F. Coward and F. J. Hartwell,[49] in a preliminary communication, stated that the lower limit of upward hydrogen flame propagation was but little affected by the presence of nitrogen peroxide, nor was the downward propagation in methane, thus suggesting that a surface phenomenon might be the determining factor. Methane did, however, show a marked decrease in the upward propagation, although not as much as might have been expected. A. C. G. Egerton,[50] in discussing Hinshelwood's results, suggests that the reaction may be explained on lines analogous to Semenoff's reasoning: the nitrogen peroxide undergoes a reaction and produces a number of thermally activated reaction centres, which can then promote chains throughout the gas, and if a sufficient number are produced explosion will occur. The suggestion was made that the higher limit might be due to some reaction product acting as an inhibitor, but it is difficult to see why a sharp limit should be expected on this view. R. N. Pease and P. R. Chesebro [51] have examined the slow combustion of methane, hydrogen, and *iso*butane in Pyrex-glass tubes, and conclude that reaction centres develop in the body of the gas and that not only does glass packing decrease the volume of free space necessary for the development of the reaction centres, but also that these are deactivated on striking the glass.

Pólányi and others [52] have made a study of chemically induced chain reactions. Hydrogen containing a small quantity of sodium vapour, acquired by passage over the molten metal, was led into chlorine, whereby some sodium chloride was formed and a considerable quantity of hydrogen chloride. This result is considered to be due to a reaction chain similar to the Nernst photochemical reaction chain :

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[49] *Trans. Faraday Soc.*, 1928, **24**, 703.

[50] *Ibid.*, p. 697.

[51] *Proc. Nat. Acad. Sci.*, 1928, **14**, 472; **A.**, 845.

[52] M. Pólányi and S. von Bogdandy, *Z. Elektrochem.*, 1927, **33**, 554; **A.**, 1928, **373**; M. Pólányi and H. Beutler, *Naturwiss.*, 1925, **13**, 1711.

$$\begin{aligned} Na + Cl_2 &\longrightarrow NaCl + Cl, \\ Cl + H_2 &\longrightarrow HCl + H, \\ H + Cl_2 &\longrightarrow HCl + Cl. \; . \; . \; . \end{aligned}$$

The chain length is estimated to be 700—10,000 molecules. Increase in sodium vapour pressure decreases the length of chain, but impurities and the glass walls have a very large effect. Potassium gave similar results with shorter reaction chains, and with methane, methyl chloride was formed, but the chain length was reduced to 100—300. The inhibiting effect of bromine was noticed and discussed more fully in a later paper.[53] The atom chain is considered to be broken by the bromine combining with the hydrogen atom, and an analysis of the chain length supports this view.

Induction by bivalent metals is of particular interest. The direct reaction $M^{II} + Cl_2 \longrightarrow MCl_2$ does not take place, but rather $M^{II} + Cl_2 \longrightarrow MCl + Cl$, and thus the chain is started. It was shown in a rather ingenious manner that the chain was not started by the activated MCl_2 molecule, although some MCl_2 is formed in the case of zinc. Cadmium causes less induction, for a greater number of atoms reach the wall without reacting with chlorine and there form cadmium chloride with no activation. Altering the pressure of hydrogen and admitting nitrogen confirmed this view and probably the reaction between Zn (or Cd) and Cl_2 does not, like that with sodium, take place at every collision. A study of the energies of activation and the heats of formation of the monochlorides led to the conclusion that these were sensibly the same, a further proof of the correctness of the mechanism.

The chemiluminescence of the " highly dilute flames " of sodium in iodine, chlorine, and mercuric chloride has been examined by various workers.[54] The theory outlined above and the kinetics and energy relations are further developed, as also is the reaction with diatomic sodium vapour. The heat of dissociation of sodium is calculated from the results to be 18 ± 2 kg.-cals. It is now certain that the reaction K + I (or Na + I) can only take place on the surface and not in the bulk phase.

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[53] M. Pólányi, *Trans. Faraday Soc.*, 1928, **24**, 606; **A.**, 1336.

[54] M. Pólányi and G. Schay, *Z. physikal. Chem.*, 1928, [*B*], **1**, 30; **A.**, 1339; *Z. Physik*, 1928, **47**, 814; M. Pólányi and S. von Bogdandy, *Z. physikal. Chem.*, 1928, [*B*], **1**, 21; **A.**, 1339; M. Pólányi and H. Beutler, *ibid.*, p. 3; **A.**, 1331; H. Ootuka and G. Schay, *ibid.*, p. 62; **A.**, 1339. (It may be noted that J. M. Walter and S. Barratt, *Proc. Roy. Soc.*, 1928, [*A*], **119**, 257; **A.**, 812, and D. S. Villars, *Proc. Nat. Acad. Sci.*, 1928, **14**, 509; **A.**, 1165, have produced evidence showing that sodium vapour at lower temperatures is largely diatomic.)

V. Kondratéev [55] has studied the reaction between sodium or potassium vapour and cupric chloride or bromide vapour at 300°. The light emitted has the same spectrum as the corresponding cuprous halide, and the reaction is believed to be a wall reaction between solid cupric halide and gaseous alkali metal giving solid alkali halide and gaseous cuprous halide. The reaction between sodium and mercuric chloride vapours is now definitely proved to be homogeneous. It may be noted that Wanklyn's original experiment [56] (compare Cowper [57]) on the distillation of sodium through dry chlorine without reaction has been repeated and confirmed, thus presenting afresh the problem of the origin of the necessary reaction centres for these chain reactions.

Combustion and Flames.

A number of papers on this subject deal with catalytic reactions, *e.g.*, with the action of anti-knocks.[58] Of particular interest is the discussion on ionisation in flames, which is treated at some length. The question as to whether the ionisation is a primary or secondary phenomenon seems to be unsolved. C. N. Hinshelwood [59] contends that " in general, chemical change is in no way dependent upon, or necessarily accompanied by anything more than a small ionisation of a secondary or accidental character." He quotes a number of experiments in support of this view, and also the work of O. W. Richardson and M. Brotherton [60] where a liquid alloy of sodium and potassium reacting with carbonyl chloride does seem to give a real large chemical ionisation. The work of Busse has been mentioned previously.[39] There can be only one view as to the small amount of ionisation produced, but it is doubtful if incontrovertible proof of its unimportance can be given. Bone quotes the well-known work of W. M. Thornton [61] on the minimum spark energy required to ignite a given mixture, which has been continued and greatly extended by G. I. Finch and L. G. Cowen [62] in a special study of the reaction when the combustion is primarily determined by the amount of ionisation. In essence their results show that when this is the case the combustion at the cathode is directly proportional to the number of ions arriving at the cathode in a given time. Bone and Townend conclude that "it is difficult to resist the conclusion that non-explosive combustion which has been taking place in both the cathode and inter-electrode zones was primarily determined by the ionisation of the gaseous medium through which the current passed and was independent of purely thermal factors." Finch and Cowen point out that the heat source of ionisation causes cumulative ionisation, which may lead to ignition and explosion at a high enough concentration. The well-known lags in some ignition phenomena may be due to these causes. E. Taylor Jones,[63] in a very recent review of the subject, has expressed the view that the best explanation of ignition by sparking is to regard it as purely thermal.

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[55] *Z. Physik*, 1928, **48**, 310; **A.**, 811.

[56] Wanklyn, *Chem. News*, 1869, **20**, 271. [57] Cowper, *J.*, 1883, **63**, 153.

[58] The earlier work is excellently summarised in W. A. Bone and D. T. A. Townend's book, " Flame and Combustion in Gases," Longmans, 1927.

[59] *Ann. Reports*, 1927, **24**, 317.

[60] *Proc. Roy. Soc.*, 1927, [*A*], **115**, 20; **A.**, 1927, 713.

[61] *Ibid.*, 1914, [*A*], **90**, 272; **91**, 17; 1915, [*A*], **92**, 9, 381; *A.*, 1914, ii, 524, 834. [62] *Ibid.*, 1926, [*A*], **111**, 257; **A.**, 1926, 690.

The probability of some electrical effects in the fixation of nitrogen by the air process has also been mentioned in Bone and Townend's book, and Bone, Townend, and Newitt believe this to be the case. H. B. Dixon, C. Campbell, and W. E. Slater [64] could find no effect at all on applying a magnetic field to explosive mixtures, and consider that there is no ground for assuming the velocity of the explosion waves to be due to the ionising action of electrons. A. E. Malinovski [65] considered he had obtained experimental evidence in support of the view that electrons conditioned explosion by applying a field between two electrodes; for hexane–air mixtures the explosion was prevented, but not for acetylene–air and hydrogen–air mixtures. In an examination of the action of anti-detonant action G. L. Wendt and F. V. Grimm [66] were unable to repeat these results, as also was S. C. Lind.[67] The most important work of W. E. Garner and S. W. Saunders [68] clarified the position to some extent. Taking several published results for the number of ions present, they applied the Saha equation and showed that in these cases no more ions were present than might have been expected. Lind [69] also supported this view. Since then, many studies have been made of ionisation in flames, but it is doubtful at the moment if it is safe to describe it definitely either as a secondary or a primary phenomenon. Without going deeply into the question of "anti-knock" action, we may quote Bone and Townend: "Two principal hypotheses, the one ionic, the other chemical, have been advanced to explain knock, and anti-knock, but neither of them is free from difficulty, and as the subject is still in a very experimental and speculative stage, the wise will ponder and scrutinise carefully such facts as have been proved or alleged, but will keep an open mind to their interpretation." Lind [70] believes there is less evidence for anti-knock action being connected with ionisation phenomena than for flame propagation with the same cause.

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[63] *Phil. Mag.*, 1928, [vii], **60**, 1090.

[64] *Proc. Roy. Soc.*, 1914, [*A*], **90**, 506; *A.*, 1914, ii, 708.

[65] *J. Chim. physique*, 1924, **21**, 469; *A.*, 1925, ii, 182.

[66] *Ind. Eng. Chem.*, 1924, **16**, 890.

[67] *J. Physical Chem.*, 1924, **38**, 57; *A.*, 1924, ii, 241.

[68] *Trans. Faraday Soc.*, 1926, **22**, 281; **A.**, 1926, 654.

[69] *Ibid.*, p. 290; **A.**, 1926, 690; Lind and D. C. Bardwell, *J. Amer. Chem. Soc.*, 1928, **50**, 745; **A.**, 455. (Compare also Marx, "Handbuch der Radiologie: Flammenleitung," Leipzig, A.V.m.b.H., 1927.)

Of the papers which have appeared during 1928, several are of considerable importance—in particular a series of papers by Semenoff and others. D. M. Newitt [71] has published a review of the large amount of data accumulated on high-pressure explosions of mixtures, and has published revised figures for the maximum pressure and temperature reached: these revised values are in agreement with the extent of dissociation of steam and carbon dioxide. W. E. Garner and C. H. Johnson [72] have examined the effect of catalysts on the speed of flame, the infra-red emission, and ionisation during the combustion of carbon monoxide and oxygen. Water vapour increased the flame speed ten-fold and reduced the radiation to about one-fourth. Nitrogen peroxide behaved as a feebly positive catalyst in a dried mixture, and as a negative catalyst in an imperfectly dried mixture.

In the dry gases it was shown that there were two waves of ionisation in the explosion wave, the first being coincident with the explosion point and the second behind it. The suggestion was made that the secondary emission of radiation was due to recombination of those ions produced behind the wave front.

N. R. Dhar [73] considers that ionisation is of common occurrence in exothermal changes, and that it could usually be detected if precautions were taken to measure it before recombination set in. He shows how many types of changes can be explained from the point of view of generation of ions, when the ions and electrons thus produced are absorbed to activate the reacting substances. He makes the point that most activated gases have a very high ionising potential, and that therefore thermal ionisation would be very difficult.

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[70] "The Chemical Effects of α-Particles and Electrons," Chemical Catalog Co., N.Y., 1928.

[71] *Proc. Roy. Soc.*, 1928, [*A*], **119**, 464; **A.**, 847.

[72] *J.*, 1928, 280; **A.**, 375; see also Garner and F. Roffey, *Nature*, 1928, **121**, 56; **A.**, 105.

[73] *Trans. Faraday Soc.*, 1928, **24**, 565; **A.**, 1335.

A. G. White,[74] in a series of papers, has examined the flame speeds in mixtures of carbon disulphide, air, and another combustible substance, such as light petroleum. The law of flame speeds breaks down when applied to mixtures. K. Yumoto [75] has made a study of the velocities of flames in carbon monoxide and hydrogen in excess of air.

A number of papers on anti-detonants have appeared. E. W. J. Mardles [76] published a very useful account of the action of lead tetraethyl in delaying explosion, and several other authors [77] have published papers on this matter. J. A. J. Bennett and Mardles [78] found greater ionisation in drops than in vapour, with a correspondingly lower ignition temperature. They suggest that a thermionic emission occurs at the moment of ignition, followed during combustion by the liberation of ions from the centres of chemical change so formed.

Two papers on high-pressure explosion have recently been published from Professor Bone's laboratory. The first [79] is a continuation of the work on explosion of mixtures of carbon monoxide and hydrogen with oxygen. The hydrogen must exceed 0·65% to give any effect, and then gives a sort of knock effect; the initial addition of hydrogen is a definite catalyst, but after the first 1% there is merely an additive acceleration; steam accelerates the reaction in somewhat the same way, but to a less extent than an equivalent amount of hydrogen, which appears to have a greater catalytic effect. In the second,[80] data are given on the effects of moisture on the explosion of carbon monoxide and steam. The effect of drying is to lower the explosion range at these high pressures, and the range can be widened by altering the temperature.

H. B. Dixon [81] has pointed out the complexity of the effects of steam on carbon monoxide–air mixtures. It is admitted now that 5—6% of steam gives the greatest rate of the explosion wave at ordinary pressures for carbon monoxide Knall-gas, whereas Bone has shown that a trace of steam catalyses the reaction and 1% of steam gives the maximum rate. It is pointed out that the greater efficacy of hydrogen than of steam had been shown earlier at Sheffield and by Dixon himself, and that in the dry mixtures the difficulty was to start the flames. He has now shown that the effect of steam and hydrogen depends entirely on the pressure. The complexity of these reactions becomes increasingly revealed upon further investigation.

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[74] *J.*, 1928, 751; **A.**, 597.

[75] *Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, **7**, 93; **A.**, 1193.

[76] *Nature*, 1928, **121**, 424.

[77] *E.g.*, Y. Nagai and M. Furihata, *J. Soc. Chem. Ind. Japan*, 1927, **30**, 781; **A.**, 1928, 847; Y. Tanaka and Y. Nagai, *ibid.*, 1928, **31**, 20; **A.**, 847; Y. Nagai, *Proc. Imp. Acad. Tokyo*, 1927, **3**, 664; **A.**, 1928, 372; P. Dumanois, *Compt. rend.*, 1928, **186**, 292; **A.**, 248; R. Duchène, *ibid.*, p. 220; **A.**, 248.

[78] *J.*, 1927, 3155; **A.**, 1928, 137.

[79] W. A. Bone, D. T. A. Townend, and G. A. Scott, *Proc. Roy. Soc.*, 1928, [*A*], **120**, 546; **A.**, 1193.

[80] W. A. Bone, D. M. Newitt, and C. M. Smith, *ibid.*, p. 563; **A.**, 248.

[81] *Nature*, 1928, **122**, 805; **A.**, 1332.

Pressures in gaseous explosions have also been studied by G. B. Maxwell and R. V. Wheeler and by W. T. David and B. H. Thorp,[82] and reference may be made to a symposium on the subject of combustion.[83] Also, Bone, Townend, and Finch contributed a summary of the present position of flame and combustion to the World Power Fuel Conference in London (September, 1928).

Semenoff's paper [84] contains a generalised view of the possible mechanism of combustion, and he shows how the cases of slow, steady combustion and explosion may both be explained by reaction centres and branched chains. If the reaction centres are removed by the walls at the same rate as they are formed, the reaction will, of course, be uniform, but if in a given volume element sufficient heat is produced to generate a large number of reaction centres, or in fact if the chains branch to a large extent, explosion will occur. Equations are given which fit the facts with some accuracy.

Assuming the Arrhenius equation, Semenoff calculates the amount of heat evolved per second, when the heat set free raises the temperature and increases the reaction velocity, and also the amount of heat lost to the walls of the vessel; he also considers the cases where explosion will occur. He shows that there must be a critical temperature of the walls of the flask for a given pressure of the gas mixture, which is confirmed by work of A. B. Sagulin on chlorine monoxide and pentane–oxygen mixtures.

In another case he considers the activation of molecules and chains. The reaction $A + B \longrightarrow AB'$ can only occur thus :

$$A' + B \longrightarrow AB';$$

AB′ can lose its energy in two ways : (1) as kinetic energy to another molecule,

$$AB' + A = AB + A,$$

or

$$AB' + B = AB + B,$$

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[82] *J.*, 1928, 15; **A.**, 248; *Nature*, 1928, **121**, 420; **A.**, 372.

[83] W. E. Garner, *Ind. Eng. Chem.*, 1928, **20**, 1008; D. S. Chamberlin and A. Rose, *ibid.*, p. 1013; Chamberlin and D. R. Clarke, *ibid.*, p. 1026; F. W. Stevens, *ibid.*, p. 1018; R. V. Wheeler and G. B. Maxwell, *ibid.*, p. 1041; T. E. Layng and M. A. Youker, *ibid.*, p. 1048; Layng and R. Soukup, *ibid.*, p. 1052.

[84] *Z. Physik*, 1928, **48**, 571; **A.**, 847.

or (2) by collision of the second kind,

$$AB' + A = AB + A'.$$

If the probability of this second process is β, and the numbers of molecules of A and B per unit volume are a and b respectively, the mean number of molecules A′ which are formed by the change $AB' \longrightarrow AB$ is

$$\alpha = \beta a/(a + b)$$

which is less than unity. If A is diatomic, however,

$$\begin{aligned} &A' + B \longrightarrow AB', \\ &AB' + A_2 \longrightarrow AB + A' + A', \\ \text{and}\qquad &AB' + A_2 = AB + A_2, \\ &AB' + B = AB + B; \end{aligned}$$

here $\alpha = 2\beta a/(a + b)$ and α may be greater than unity.

If the concentration of AB′ is c', that of A′ is a', and that of AB is c, and the total number of molecules in unit volume $= a + b = n$,

$$da'/dt = - Za'b + \beta Zac' + n_0 = - Za'b + \alpha Znc' + n_0 \qquad (1)$$

where $Z =$ the total number of all types of collision, it being assumed that all molecular diameters are equal;

$$dc'/dt = Za'b - Zc'n \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$w = dc/dt = Zc'n$$

where w is the reaction rate, and n_0 is the number of activated atoms of A′ which are formed in unit time by thermal vibration and black radiation.

From Arrhenius's theory the number of active A′ atoms per unit volume $= x_0 = ae^{-E/RT}$ and $n_0 = x_0/\tau$, where τ is mean life of A′.

Integrating equations (1) and (2) and assuming that α is nearly 1, we have

$$\alpha < 1, \quad w = \frac{n_0}{1 - \alpha}\left[1 - e^{-\frac{Zbn(1 - \alpha)t}{b + n}}\right] \quad . \quad . \quad . \quad (a)$$

$$\alpha > 1, \quad w = \frac{n_0}{\alpha - 1}\left[e^{\frac{Zbn(\alpha - 1)t}{b + n}} - 1\right]. \quad . \quad . \quad . \quad (b)$$

$$\alpha = 1, \quad w = \frac{Zbnn_0}{b + n}t.$$

When t is infinite, and $\alpha < 1$, $w_\infty = n_0/(1 - \alpha)$

and when $\alpha \geqslant 1$, $w_\infty = \infty$;

and hence as long as $\alpha < 1$ a steady reaction is possible, but in the other cases the reaction rate increases indefinitely. Since α is a function of the pressure of oxygen, the condition $\alpha \geqslant 1$ determines the critical range for the explosion.

At a constant pressure of phosphorus vapour the critical pressure does not change with the temperature, and therefore in collisions of the second kind the energy quantum transformation must be much greater than the mean kinetic energy of motion, and this constitutes the difference between reactions of this type and the reaction of the explosion type where the critical pressure increases with temperature according to $e^{-E/RT}$.

A. B. Sagulin [85] has examined the minimum pressures for explosion of mixtures of H_2 and Cl_2 or Br_2; Cl_2 and O_2, Cl_2O, CH_4, C_2H_6, C_3H_6, C_5H_{12}, CO, and H_2, and finds that in all cases the expression $\log P/T = A/T + B$ (compare Semenoff) is obeyed. A is a constant for the given reaction and independent of the bulb size; B depends on the bulb size, and has a minimum value as a rule at 66% of either component. Some of the above reactions are regarded as purely thermal.

A complete account of the " hydroxylation " theory to account for preferential combustion has been given by Bone and Townend, who sum up the position by stating that if the theory is not applied too rigidly it will be found to account for the facts better than any other theory, though they consider it to be incomplete in its present form. They do not consider an oxygenated molecule to be disproved, in which connexion the discussion by Egerton [86] is of interest. He takes the view that peroxidation is the initial cause of combustion, in much the same way as Bäckström's mechanism. In his Royal Institution lecture he reviews the position, with special reference to peroxidation. W. A. Bone [87] restates the hydroxylation theory and facts supporting it, to which Egerton in principle agrees. F. Gill, E. W. J. Mardles, and H. C. Tett [88] have examined the flames or phosphorescent glow produced when slow combustion takes place, with special reference to autocatalysis and inhibitors. They observe, *inter alia,* that their results support the view that nuclear particles are formed prior to oxidation, and these particles, probably ionised, form the centres of chemical change. Their general position is that peroxidation is the general cause of phosphorescence, autocatalysis, and detonation in a petrol engine, and that inhibitors act by removing the active oxygen and energy from these primarily formed peroxides.

K. F. Bonhoeffer and H. Reichardt [89] have shown from the absorption spectra of steam containing oxygen at 1200° that free hydroxyl is present. In the equation $2H_2O = H_2 + 2OH - 125{,}000$ cals. (at 1400°) the 125,000 is considered to be a minimum value, and calculation on the Nernst equation gives results near those experimentally determined.

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[85] *Z. physikal. Chem.*, 1928, [*B*], **1**, 275.

[86] *Nature*, 1928, **121**, 10; **A.**, 137; **122**, 20, 204.

[87] *Ibid.*, p. 204; **A.**, 960.

[88] *Trans. Faraday Soc.*, 1928, **24**, 574; **A.**, 1335.

[89] *Z. Elektrochem.*, 1928, **34**, 652; **A.**, 1188.

E. Gaviola [90] has recently published three papers on optical excitation by mercury. In a study of the photosensitised band fluorescence of OH and other molecules, he has examined the production of free hydroxyl in some detail. When a few millimetres of water vapour are introduced into a tube containing excited mercury vapour, HgH and OH bands appear. H. Senftleben and (Frl.) I. Rehren [91] had concluded that the dissociation of H_2O into H and OH had to correspond to less than 4·9 volts, but Gaviola and R. W. Wood [92] conclude that the energy must exceed this, with a probable value of 5·20 volts. Since $H_2 \longrightarrow 2H - 4{\cdot}38$ volts, this would give $2H_2O \longrightarrow H_2 + 2OH - 6{\cdot}0$ volts (about). The OH molecule is believed to have a mean life of about 0·01 sec. under the conditions of the experiment. About one collision in 10,000 between water and metastable mercury is effective in producing hydroxyl.

K. F. Bonhoeffer and F. Haber [93] have also examined the evidence for the free hydroxyl radical and its part in flame production. Prior to Gaviola, Reis, Watson, and Mecke [94] had studied the question to some extent, and this earlier work is summarised. There is now no doubt that the hydroxyl radical is the emitter of the λ 3064 band, and Haber and Bonhoeffer have fully examined the energy relations from both spectral data and thermochemical work. They consider that

$$H_2O = OH + H - 5 \text{ volts},$$

which is in good agreement with the later work of Gaviola. Applying Hess's law also, they obtain as a mean value,

$$O + H = OH + 5{\cdot}35 \text{ volts},$$

or from the spectral data of Birge and Sponer,

$$O + H = OH + 5{\cdot}26 \text{ volts}.$$

This paper was also continued to consider the energy relation when carbon and hydrocarbons were present.

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[90] *Phil. Mag.*, 1928, (7), **6**, 1154.

[91] *Z. Physik*, 1926, **37**, 529; **A.**, 1926, 768.

[92] *Phil. Mag.*, 1928, (7), **6**, 1191 (compare S. Mrozovski, *Z. Physik*, 1928, **50**, 657; **A.**, 1304).

[93] *Z. physikal. Chem.*, 1928, [*A*], **137**, 263.

[94] A. Reis, *ibid.*, 1914, **88**, 513; *A.*, 1915, ii, 257; W. W. Watson, *Astrophys. J.*, 1924, **60**, 145; *A.*, 1925, ii, 349; R. Mecke, *Z. Physik*, 1927, **42**, 390.

More recently still, K. Tawada and Garner,[95] accepting this, have shown how the presence of hydroxyl radical in flames will alter the total radiation. Measuring the total radiation from hydrogen and oxygen mixture, they showed that maximum emission occurs near $H_2 + O_2$ and not at the highest temperature, given by $2H_2 + O_2$. Assuming that $H_2 + O_2 \longrightarrow 2OH$ is the primary reaction, and the hydroxyl may emit a portion of its energy as chemiluminescence, this result is explained, since the life of the hydroxyl is shortened by the presence of hydrogen, and hence there should be less radiation.

Chemical Reaction by Ionisation.

Reference has already been made to the general question of ionisation in chemical change. A new edition of Lind's monograph [70] contains most of the data so far available on this subject, as well as a very complete account of most of the published work on reaction by ionisation. The view is taken that clustering is the reason for more than one reaction product being formed per ion pair, and in all cases the supposed ion cluster is given. Acetylene, forming $(C_2H_2)_{20}$, is apparently the largest cluster.

The evidence for clustering is discussed by L. B. Loeb,[96] who shows that, whilst it is not all incontrovertible, the position is better explained by clusters than by the small-ion theory. The law of Blanc, *viz.*,

$$k_c = \frac{k_a k_b}{(1 - c)k_a + ck_b}$$

where k_a is the mobility, and c and $1 - c$ the concentrations, is not universally valid, but is useful as a criterion as to the form of cluster; and consideration is given to the dielectric attraction of the molecules by the changed ion, using a fifth-power law.

He concludes that in the following mixtures there is no apparent clustering: $C_2H_2 + H_2$; $CO_2 + H_2$; $O_2 + CO_2$; $C_2H_5I + H_2$. "Statistical labile clustering" is found in $NH_3 + H_2$; $NH_3 +$ air; $SO_2 + H_2$, whilst definite clustering is shown, with a negative ion, in $Cl_2 + H_2$; $Cl_2 + O_2$; $Br_2 + H_2$; HOH or R·OH + air; with a positive ion in ether $+ H_2$; or with an ion of either sign in HCl + air; H_2S; $H_2 + I_2$. Besides the work above, H. A. Erikson [97] has continued his work on ionic mobilities by the "air blast" method, by which he can examine the ageing of the ion and the early stages of cluster formation, and his results are in support of the cluster theory. His most recent paper deals with the mobilities of ions in moist air, his conclusions being that water loses an electron to the final positive air ion, forming H_2O^+ of greater mobility, and discharges the air ion.

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[95] *Nature*, 1928, **122**, 879.

[96] *Physical Rev.*, 1928, (2), **32**, 81; **A.**, 932.

[97] *Ibid.*, p. 791; 1927, (2), **30**, 343; **A.**, 1927, 1002; 1926, (2), **28**, 372; and earlier papers.

The place of ions in combustion and in some cases of surface reaction has been or will be treated. Reactions occurring through ionisation may be appropriately mentioned here. J. E. Maisin[98] has examined the oxidation of sulphur dioxide in the presence of radon; and finds that the ratio of the number of ions disappearing to the number of ion pairs is 1·51, and hence, since sulphur trioxide is the primary product, one ion pair produces one molecule of sulphur trioxide. R. Ruyssen[99] has reasoned that the thermal decomposition of ozone occurs in two stages: (1) the breaking of the molecule into negative and positive ions, proceeding with measurable velocity according to the number of effective molecular collisions per second; and (2) the combination of the ions to O_2 molecules being instantaneous. In support of this, he shows that when the decomposition takes place in an electric field the ionisation and the decomposition are directly proportional; and the ionisation increases rapidly with the strength of the field.

Reactions with ions as the primary causative agency have been studied. R. D. Rusk[1] has studied the combination of hydrogen and oxygen in the low-voltage arc, and in a Geissler discharge. In the latter, he finds that at low pressures the number of water molecules formed is less than the number of ion pairs; but increasing the pressure tends to bring the value up to that of Lind, *i.e.*, 3·9 pairs. He suggests that combination may be due to excitation produced by a process secondary to ionisation. In the low-voltage arc, the reaction on an oxide-coated platinum filament was very rapid; and whilst application of a voltage of 74 volts and the striking of a 5 m.a. arc increased the rate of production, the difference was relatively small and could not be examined in detail. A. Caress and E. K. Rideal[2] have worked on the reactions of carbon monoxide, and carbon monoxide and hydrogen, in the low-voltage arc. Reaction is found to begin at the critical potentials of carbon monoxide.

Sagulin and A. Leipunsky[3] have recently published some work on the oxidation of mercury vapour in the presence of 5-volt electrons and show that the reaction proceeds faster when 5 volts are applied.

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[98] *Ann. Soc. Sci. Bruxelles*, 1927, [*B*], i, **47**, 172; **A.**, 1928, 104.

[99] *Natuurwetensch. Tijds.*, 1928, **10**, 101; **A.**, 953.

[1] *Physical Rev.*, 1928, (2), **32**, 287; **A.**, 1099.

[2] *Proc. Roy. Soc.*, 1928, [*A*], **120**, 370; **A.**, 1198.

[3] *Z. physikal. Chem.*, 1928, [*B*], **1**, 362; Leipunsky, *ibid.*, p. 369.

The 2537 mercury line corresponding to excitation from $1S$ to $2p_2$ corresponds to 4·86 volt electron units, the actual value observed by Franck and Einsporn being 4·9 volts,[4] and the reaction probably proceeds by excitation of the mercury atoms.

A. de Hemptinne [5] has examined the reduction of metallic oxides by hydrogen in a discharge, and it is shown that lead peroxide and mercuric oxide are reduced when not directly exposed to electronic or ionic bombardment, but copper oxide or lead monoxide is not. It is held that in the tube exists un-ionised, activated hydrogen, monatomic, triatomic, or excited. Reduction at the cathode is due to positive ions, and at the anode to negative ions or active hydrogen. E. Goldstein [5a] has studied the synthesis of ammonia in the presence of argon in a discharge tube.

Catalysis and Ionisation.

The suggestion that the relation between thermionic emission and catalysis is very intimate is now well known, and recently the tendency to ascribe catalytic phenomena to purely physical causes has increased. It has long been held that the hydrogen–oxygen reaction on a hot surface is primarily due to ionisation in some form; and of late Langmuir, Kunsman, Briner, and others have pointed out the more general connexion.

G. Owen [6] studied the pressure changes and electrical phenomena when mixtures of hydrogen and air reacted on a hot platinum wire at about 300°, and ascribed the reaction to the production of charged nuclei by the emission from the surface, which accelerated or caused the oxidation. He was unable to detect any change when fields up to 100 volts were applied, so that the existence of these charged nuclei was never clearly demonstrated. P. J. Kirby,[7] studying the reaction between hydrogen and oxygen on a heated platinum filament under better experimental conditions, could detect no appreciable reaction below a critical temperature of *ca.* 250°. He attributed the reaction to ionisation by the emitted electrons and subsequent reaction by the ions. Bone,[8] from the results of much work on explosions and gaseous combustions at hot surfaces, also suggested that the electrical emission played an important part in surface oxidation. He pictured a mechanical rôle for the surface, as a support where layers of electrified gas were held and enabled to react very quickly.

J. R. Thompson,[9] studying the same reaction, in an apparatus in

[4] *Z. Physik*, 1920, **2**, 18.

[5] *Ann. Soc. Sci. Bruxelles*, 1927, **47**, *B*, i, 143; **A.**, 1928, 139; *Bull. Acad. roy. Belg.*, 1928, (5), **14**, 8.

[5a] *Z. Physik*, 1928, **47**, 274; **A.**, 486.

[6] *Phil. Mag.*, 1903, (6), **6**, 306.

[7] *Ibid.*, 1905, (6), **10**, 467.

[8] *Rep. Brit. Assoc.*, 1910.

[9] *Physikal. Z.*, 1913, **14**, 11.

which he could also measure very small electron currents, considered that the electron emission also played a very important part in the rapid bulk reaction, culminating in explosion; and stated that at the point where explosion occurred the electron emission commenced to rise rapidly. His results are unfortunately rendered less conclusive by his failure to measure the electron emission while the reaction was taking place, since the rise in emission in a vacuum at apparently the same temperature may well be fortuitous.

I. Langmuir[10] has shown that the relation between electron emission and catalysis is very close, and cites as an example the poisoning of a surface as an emitter and as a catalyst, the two processes running parallel to each other. R. Thomas[11] suggests that the process of catalysis may be a consequence only of the emission of electrons and ionisation; he mentions many examples of good electron emitters acting as catalysts, and makes the interesting suggestion that the great influence of water vapour may be due to the formation of nuclei round any ions, in which the reaction proceeds rapidly. In a study of the combustion of hydrogen and oxygen on heated surfaces, he had observed that the reaction was rapid on barium, calcium, or strontium oxide, and corresponded roughly to the electron currents they could produce. On alumina, a poor emitter, the rate of reaction was only about one-tenth of that on the other oxides. That the mechanism could not be a simple case of one emitted electron causing one pair of molecules to react, he showed by a calculation of the saturation current, which was only of the order of 10^{-6} of that required by that view; but he suggests that ionisation may greatly increase these rates, and cites as an example the phenomenon of autocatalysis.

The very interesting work of C. H. Kunsman[12] on the properties of prepared ammonia catalysts may also be mentioned: these catalysts of magnetite with 1% of alumina, baryta, etc., give a very large positive ion emission, some 100 times as great as the electron emission at temperatures of the order of 600°. He considers that those parts of the surface which emit positive ions may be considered to act as positive reaction centres. In measurements of the rate of decomposition of ammonia on prepared catalysts, he showed that the rates could be increased four-fold by the mode of preparation of the catalyst, whilst a trace of promoter would cause an 18-fold rise, the energy of activation remaining approximately constant; so he considered that the function of the poison or promoter was merely to alter the value of A in the equation $K = Ae^{-E/RT}$. Promoters increase the number of atoms on which decomposition may take place, whilst poisoning, heat treatment, or promoters also alter the quality of the atoms which will cause the reaction.

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[10] *J. Amer. Chem. Soc.*, 1916, **38**, 2271.

[11] *J. Soc. Chem. Ind.*, 1923, **42**, 21T; *A.*, 1923, ii, 64.

[12] *J. Physical Chem.*, 1926, **30**, 525; **A.**, 1926, 685; *Science*, 1927, **65**, 527; **A.**, 1927, 1039; *J. Franklin Inst.*, 1927, **203**, 637; **A.**, 1927, 603.

He showed that the positive-ion work function ϕ_+ was always smaller than the negative one ϕ_-, and hence the surface must be considered as covered with positive ions, instead of with atoms and electrons, as O. W. Richardson and A. F. A. Young [13] showed to be more generally the case. There was always a single positive charge on the ions, and no tendency to cluster was observed. Kunsman further takes the view that the promoter may act by lowering ϕ_-, by causing new interfaces, or by assisting the emission of a positive or negative ion. In a more recent paper,[14] he has shown that the energies of activation for the decomposition of ammonia on heated nickel, molybdenum, and tungsten range from 26,000 to 45,000 cals., and hence he discards his original idea that the energy of activation was a function purely of the gas and had no connexion with the catalyst.

The parallelism between catalysis and thermionic emission is further supported by the work of Briner [15] and others, who have shown that the direct oxidation of nitrogen by platinum, and oxide-coated platinum, using lime, baryta, strontia, and their mixtures, is catalysed by these substances to a degree bearing a roughly constant ratio to their efficiency as electron emitters. The experiments are not conclusive, in that possible variations in the surface areas of the catalysts were not considered.

L. V. Pisarshevski [16] believes the catalytic action of metals to be due to freely-moving electrons, and states that adsorption of gases is due to electrostatic forces binding the gas to a film of free electrons on the surface. Ionisation occurs either in this film or in occluded gases; and he states that when these gases are re-evaporated they retain their catalytic efficiency, and can cause the thermal decomposition of potassium chlorate at a distance of 10 or 12 cm. from the metal catalyst. The effect of ultra-violet light on metal catalysts is shown to be due to the emission of photo-electrons. The reaction of hydrogen and oxygen on platinum foil, the catalytic thermal decomposition of potassium chlorate on metals and oxides, the inversion of cane-sugar, and the decomposition of albumoses and peptoses on illuminated platinum foil, are stated to be greatly accelerated by illumination and the emission of photo-electrons. In general, the catalytic activity of metals and oxides is due to activation and ionisation of adsorbed gases, which retain their activation on desorption. O. Schmidt[17] has examined the possibility of ionisation of hydrogen on a metallic catalyst, and considers it to be more likely than dissociation. Calculations on the Bohr–Kossel model and Bohr–Landé formula showed qualitatively that ionisation was possible, and was greatest on those metals having the smallest ionic radii, as, for example, nickel. His calculations are in agreement with many measurements on absorption of hydrogen.[18] Further he studied the hydrogenation of ethylene on iron, cobalt, nickel, silver, gold, zinc, and lead, and obtained catalytic efficiencies in the inverse order of the ionic radii in most cases. It is further suggested that the organic compound in a hydrogenation may also be ionised by electron addition, thus permitting an electrically neutral hydrogenation product.

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[13] *Proc. Roy. Soc.*, 1925, [*A*], **107**, 377; *A.*, 1925, ii, 343.

[14] *J. Amer. Chem. Soc.*, 1928, **50**, 2100; **A.**, 1101.

[15] E. Briner, J. Boner, and A. Rothen, *Helv. Chim. Acta*, 1926, **9**, 634; **A.**, 1926, 916.

[16] *Ukraine Chem. J.*, 1925, **1**, Sc. Part 1, and other papers.

In a later paper an expression for the adsorption in terms of the size of the pores is obtained, which deviates when a chemical reaction occurs. It is stated that when ionisation of the adsorbed gas takes place and forces of attraction additional to the van der Waals terms are called into play, the force needed for the separation of the molecules of the gas is greater than the calculated values.

The charging of a platinum foil diminishes its catalytic activity by destroying favourable conditions of equilibrium between positive hydrogen ions and negative ions on the surface. The work of G. I. Finch and J. C. Stimson,[19] who studied the charging of gold and silver surfaces heated in atmospheres of hydrogen, oxygen and other gases, is of interest in this connexion. The surfaces acquire a positive change in oxygen, and a negative change in a vacuum of the order 10^{-5}, or in hydrogen. They suggest that the gas is adsorbed and condensed on the surface into a layer of electrically neutral molecules. The first stage of this process is the formation of an unstable compound, momentarily in equilibrium with neutral molecules and the metal; this compound then dissociates giving gas molecules which have been activated by the surface, and the latter retains a charge. The charging up in a vacuum is explained by the activation and emission of the metal vapour. It is suggested that, simultaneously with this process, the gas may be activated directly. These authors find no evidence for occlusion below the surface layers. In a more recent paper the work has been extended, and the conclusions have been confirmed; at least five types of adsorption are distinguished, ranging from purely physical electrically neutral to intermediate compounds.

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[17] *Z. physikal. Chem.*, 1925, **118**, 193; **A.**, 1926, 134; 1928, **133**, 263; **A.**, 582.

[18] In particular, those of Sieverts, *ibid.*, 1907, **60**, 142; 1909, **68**, 120; Naumann and Streints, *Monatsh.*, 1891, **12**, 655; Baxter, *Amer. Chem. J.*, 1899, **22**, 362.

[19] *Proc. Roy. Soc.*, 1927, [*A*], **116**, 379; **A.**, 1927, 1135.

The early experiments of P. Anderson,[20] showing that hydrogen, after passing over hot platinum or palladium at about 250°, retained its catalytic activity and could reduce copper oxide or react with sulphur at a lower temperature than in the control experiments, and said to be due to some activated form, have usually been considered inconclusive owing to the possible contamination with oxygen. More careful experiments by Paneth [21] and by others [22] failed to reveal any production of active hydrogen by this means. M. Poljakov,[23] on the other hand, has observed that if hydrogen at low pressure is drawn over palladium, iron, or nickel at 400—800° there is no luminescence, but that if later, at a point remote from the metal, some oxygen is admitted, the reaction glow is produced, this effect not being shown by mixtures of oxygen and hydrogen.

J. W. Broxon [24] considers that there is no dependence between slow chemical action and ionisation in gases, and that chemical action has no apparent effect in increasing ionisation. The tarnishing of metals provided experimental evidence in favour of this view.

A more complete study of the ionisation effects in chemical reactions has been made by A. K. Brewer.[25] In his earlier papers he shows that equal amounts of negative and positive ions are produced in the surface reactions of ethyl alcohol and oxygen on gold and other surfaces. These can be measured, and the current is proportional to the applied voltages, no saturation being reached, and they are exponential with the temperature. He suggests that ionisation takes place only in the surface layers, and the fields cannot reach far enough down to remove all the ions, but only a small fraction. It is shown that the energy required to emit an electron is always greater than that required to cause chemical reaction.

In a review and summary of his work, he suggests a possible mechanism of this surface ionisation, based on the intrinsic field of the metal and the image field of the electron itself as it is brought up to the surface. These ions can escape and react chemically when they have sufficient kinetic energy, thus becoming thermions; but the chance of escape depends on the distance from the surface. In this way surface catalysis becomes a special case of thermionic emission, it having been shown that there is no possibility of the electron emission being due solely to chemical reaction or emission from the absorbed gas. Equations similar to the Richardson thermionic equation are derived for the reaction velocity:

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[20] *J.*, 1922, **121**, 1152.

[21] F. Paneth, E. Klever, and K. Peters, *Z. Elektrochem.*, 1927, **33**, 102; **A.**, 1927, 429.

[22] A. Bach, *Ber.*, 1925, **58** [*B*], 1388; *A.*, 1925, ii, 885; M. Scanavy-Grigorieva, *Z. anorg. Chem.*, 1926, **159**, 55; **A.**, 1927, 119; G. A. Elliott, *Trans. Faraday Soc.*, 1927, **23**, 60; **A.**, 1927, 187; H. M. Smallwood and H. C. Urey, *J. Amer. Chem. Soc.*, 1928, **50**, 620; **A.**, 493.

[23] *Naturwiss.*, 1927, **15**, 539; 1928, **16**, 131; **A.**, 1928, 459, 1308.

[24] *Physical Rev.*, 1926, **27**, 542; **A.**, 1926, 656.

[25] *J. Physical Chem.*, 1928, **32**, 1006; **A.**, 968; and several earlier papers.

$$R = n_0\left(\frac{KT}{2\pi m}\right)^{\frac{1}{2}} e^{-\frac{W_1 + W_2 + W_3 + W_4}{KT}},$$

where W_1 = work done by ions and image field;
W_2 = work done by intrinsic field on ions;
W_3 is a measure of the effect of pressure on the emission of ions;
W_4 = work required to complete the dissociation;
R = rate at which a given ion escapes into the chemically active region;
n_0 = ionic concentration at the surface;
m = mass of ion.

This in general reduces to the form

$$\text{Rate of forward reaction} = dc'/dt = A_1 T^{n'/2} e^{-b'/T}$$

where n' is the number of ions contributing to the forward reaction, and b' includes the W factors of all the reactants. A similar expression is obtained for the back reaction

$$dc''/dt = A_2 T^{n''/2} e^{-q/T}$$

and for equilibrium

$$K = A T^{(n'' - n')/2} e^{-(q - b')/T}$$

This expression is shown to be in agreement with Brewer's own work, and compatible with the " active patch " theory, W_2 being sensitive to changes in these.

In general these ideas are similar to those of (Sir) J. J. Thomson,[26] but the treatment is more extended.

Further references to this subject are given by Hinshelwood.[59]

Surface Condensation.

Until recently it had been tacitly assumed that the rate of evaporation of an adsorbed film was independent of the surface concentration, and that there was no lateral movement of the adsorbed molecules over the surface of the adsorbing solid; but as a result of investigations on the condensation of metal vapours, information has been obtained showing that these views must be modified. R. W. Wood [27] showed that critical temperatures existed for the condensation of mercury, cadmium, and iodine on glass surfaces, and that the reflexion of atoms from the surface above the critical temperatures followed the cosine law. M. Knudsen,[28] in a similar investigation with mercury, obtained comparable results. Langmuir [29] first discussed the possibility of forming condensation nuclei of mercury which would serve as starting points for the formation of deposits at surface temperatures much above those obtaining when nuclei were absent. I. Estermann and M. Volmer,[30] in considering the growth of a crystal by condensation of molecules from the vapour, suggested that when a molecule enters the field of force at the surface of a crystal it remains there for a certain "life" time, after which it may re-evaporate, be added to the edge of the crystal, or coalesce with others to build up a new lattice plane. In the experimental part of this work it was shown that the reflexion coefficient α for mercury vapour on liquid mercury was unity and independent of the temperature, but for solid mercury it was less than unity. Volmer, with several other workers, has elaborated these ideas.[31] A crystal should grow 1000 times faster in one direction than another if the molecules adhered to the point on the lattice where they struck; and therefore the molecules must either be able to penetrate the crystal or, more probably, are adsorbed on the surface and can then migrate. Evidence was brought forward [32] that this was probable for mercury vapour adsorbed on solid mercury and for benzophenone on glass surfaces. In the latter case the frictional resistance in the two-dimensional gas was found to be about 100 times that of an aqueous solution. Microphotographs gave further support to this suggestion. The nuclei formation in supersaturated states, and crystalline formation from vapours, solutions, etc., were also studied.[33] Estermann and Volmer [34] have shown by an ultramicroscope that the evaporated layer consists of a great number of small crystals.

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[26] " The Electron in Chemistry," Chap. 4.

This lateral mobility over a surface—if, indeed, it exists in the case of adsorbed vapours and gases—is evidently a factor of great importance in heterogeneous catalysis, for active patches or reactive interfaces may be kept supplied with reactants, not only by condensation from the gas phase, but also by lateral migration.

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[27] *Phil. Mag.*, 1915, **30**, 300. [28] *Ann. Physik*, 1916, **50**, 472.

[29] *Proc. Nat. Acad. Sci.*, 1917, **3**, 141.

[30] *Z. Physik*, 1921, **1**, 13.

[31] M. Volmer, *ibid.*, 1922, **9**, 33, 193; *Physikal. Z.*, 1921, **22**, 646.

[32] M. Volmer and G. Adhikari, *Z. Physik*, 1925, **35**, 170; **A.**, 1926, 349; *Z. physikal. Chem.*, 1926, **119**, 46; **A.**, 1926, 467.

[33] M. Volmer and A. Weber, *ibid.*, p. 277; **A.**, 1926, 676.

The mechanism of building up a new layer of condensation has been investigated by several workers [31, 34, 35, 36] and theoretically by J. Frenkel.[37] It has been shown that the so-called critical temperature of condensation varies with the stream density of the metallic beam. Frenkel adopts the hypothesis that a condensed atom remains in the adsorption field for a definite life time, and during its life at the surface it moves about in the manner of a two-dimensional gas. If, during this motion, it collides with another atom, a doublet is formed which can act as a condensation nucleus for other atoms. According to these assumptions, the life of an atom on the surface is longer in the doublet form than as a single atom, and is also dependent on both the energy of adsorption and the temperature of the surface, this life τ being given by

$$\tau = \tau_0 e^{U/KT}$$

where U is the energy of adsorption.

If n is the total number of adsorbed atoms on the surface per unit area, the number of isolated atoms will be $n_1 = n(1 - n\sigma)$, and of paired atoms $n_2 = n^2\sigma$, where σ is the effective area of the field. If the stream density is ν, the rate of evaporation will be

$$dn/dt = \nu - n/\tau + \sigma n^2/\tau'',$$

τ'' being the life of an atom in the doublet. In the stationary condition $dn/dt = 0$, and this corresponds to the critical condition for the value of ν above which condensation will take place.

From Chariton and Semenoff's data for the relationship between the critical stream density and the temperature of condensation of cadmium on a mica surface, the work of evaporation of paired atoms is 11,000 cals. per g.-mol. From Langmuir's work on the adsorption of oxygen on tungsten, a value of 170,000 cals. is found. Cockcroft has found 5,700 cals. for the evaporation of paired cadmium atoms on copper, and about 2,000 cals. for the heat of dissociation of the surface doublets, but the true surface forces were probably masked by adsorbed gas films. He also obtained definite proof of the surface diffusion of deposited cadmium atoms. Pólányi [38] has applied the Frenkel relation $q = 15T$ to the case of

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[34] I. Estermann, *loc. cit.*; *Z. Physik*, 1925, **33**, 366; *Z. Elektrochem.*, 1925, **31**, 441; *A.*, 1925, ii, 1053.

[35] J. Chariton and N. Semenoff, *Z. Physik*, 1924, **25**, 287; *A.*, 1924, ii, 723.

[36] J. D. Cockcroft, *Proc. Roy. Soc.*, 1928, [*A*], **119**, 295; **A.**, 945.

[37] *Z. Physik*, 1925, **33**, 366.

[38] *Chem. Rund. Mitteleuropa Balk.*, 1927, **4**, 160; *Chem. Zentr.*, 1928, 285; **A.**, 718.

catalytic acceleration of hydrogen molecules from atomic hydrogen on glass walls. He finds q, the adsorption potential, to vary from 1,500 g.-cal. for wet glass to 40,000 for metals. Clausing,[39] in a similar manner, showed that the life of an argon molecule on a glass surface varied exponentially with the temperature, obtaining $\tau = 0{\cdot}93 \times 10^{-11} e^{2430/RT}$ second.

On thoriated filaments used as thermionic emitters, such surface mobility appears evident.[40]

Three types of adsorption of vapours by solid surfaces are now distinguished: (1) the unimolecular film, in many cases tenaciously held, as first definitely suggested by Langmuir; (2) capillary condensation in micropores of a porous substrate, as imagined by Zsigmondy and Patrick; and (3) the building up of multimolecular layers on a plane surface, suggested by Eucken, Pólányi,[41] and de Boer.[42] The experimental evidence in favour of the first two processes is reasonably convincing, but investigations on the existence of multimolecular layers on plane surfaces have led to apparently conflicting results. The extension of the work of I. R. McHaffie and S. Lenher[43] by G. H. Latham[44] appears to indicate that multimolecular films may be formed on rough, but not on smooth, surfaces. The necessity for roughening the silver thimble in a dew-point apparatus, and the behaviour of a spreading oil when poured on water in quantities sufficient to form more than a unimolecular layer, may be pertinent in this connexion. Despite the great number of adsorption isotherms proposed, it cannot be said that any one will be found completely satisfactory, and none is competent to explain the isotherms of water and alcohols on alumina, silica, silica gel, or ferric oxide. It is suggested by A. Fleischer[45] that this type of curve is generally possible for adsorption of vapours, and that none of the above theories alone will explain it satisfactorily; but in many cases a combination of surface adsorption and capillary condensation will give a reasonable explanation.

That adsorption on surfaces might be due to nothing more than electrostatic attraction effected by the mirror image of the permanent dipole of the vapour in the adsorbent, was suggested by Eucken. This concept of a mirror-image attraction of a permanent or induced dipole or pole of higher order has been extended by R. Lorenz and A. Landé,[46] Jacquet,[47] and H. Cassel.[48] In general, the changes in potential energy effected in this way are small, with the result that attempts have been made to investigate the possible effect of the intrinsic field as well as the mirror-image field of the solid adsorbent on the molecules undergoing absorption.

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[39] Thesis, Amsterdam, 1928.

[40] Schottky and Rothe, "Handbuch der Experimentalphysik," XIII, Teil 2, Leipzig, 1928.

[41] F. Goldmann and M. Pólányi, *Z. physikal. Chem.*, 1928, **132**, 321; **A.**, 579. Compare also E. Hückel, "Adsorption und Kapillarkondensation," A.V.m.b.H., Leipzig, 1928.

[42] *Physica*, 1928, **8**, 145.

[43] *J.*, 1925, **127**, 1559; 1926, 1785; compare J. C. W. Frazer, W. A. Patrick, and H. E. Smith, *J. Physical Chem.*, 1927, **31**, 897; **A.**, 1927, 722.

[44] *J. Amer. Chem. Soc.*, 1928, **50**, 2987.

[45] *Amer. J. Sci.*, 1928, **16**, 247; **A.**, 1086.

The simple treatment of J. H. de Boer [42] gives values for the deformation of iodine adsorbed on calcium fluoride which are of the right order of magnitude, whilst O. Blüh and N. Stark [49] and J. E. Lennard-Jones and (Miss) B. M. Dent [50] have evaluated the field outside a heteropolar crystal such as sodium chloride. On surfaces such as metals and metallic oxides the modifications in the double layer potentials effected on adsorption of various substances have been investigated in some detail by studies of photoelectric and thermionic emission of electrons. It is here that the intrinsic field can be examined with the greatest certainty, and the recent work in this particular field by Langmuir, Kingdon, Dushmann, Becker, and others, which has been ably summarised by Schottky and Rothe,[40] is clearly closely akin to the problem of surface action.

Molecules adsorbed from solution are believed by van Duin,[51] in agreement with Kruyt and others, to be in a less favourable condition to take part in a reaction. Working with racemic and *meso*-dibromosuccinic acid and potassium iodide, the rate is increased by adsorbent carbon, and in this case the reacting group is turned away from the adsorbent into the liquid, but the velocities of hydrolysis of some eight varied substances examined were much reduced, as also was that of the reaction of racemic dibromosuccinic acid to form bromofumaric and hydrobromic acids. Van Duin states that the orientation must be sufficiently favourable to overcome the primary decrease in reaction velocity caused by adsorption, if it is to increase, and there may thus be two compensating influences.

R. N. Pease and L. Stewart [52] have examined the relation between the catalytic activity and adsorption of supported metal catalysts—iron, cobalt, nickel, and copper—on hydrogen and ethylene.

[46] *Z. anorg. Chem.*, 1922, **125**, 47; *A.*, 1923, ii, 13.

[47] "Theorie der Adsorption von Gasen," 1925.

[48] *Physikal. Z.*, 1927, **28**, 152; **A.**, 1927, 314.

[49] *Z. Physik*, 1927, **43**, 575; **A.**, 1927, 929.

[50] *Trans. Faraday Soc.*, 1928, **24**, 92; **A.**, 8.

[51] *Rec. trav. chim.*, 1928, **47**, 715.

[52] *J. Amer. Chem. Soc.*, 1927, **49**, 2783; **A.**, 1928, 29.

F. H. Constable,[53] G. Tammann and K. Bochov,[54] and U. R. Evans [55] have examined the formation of oxide films on metal surfaces, and the first has extended his work to evaluate the area of the surface oxidised, using spectrophotometric measurements of the thickness of the film, and simultaneous measurements of the electrical conductivity of the film and of the amount of oxygen absorbed. Metal films were deposited electrolytically on graphite, and the areas of iron, nickel, and copper accessible to oxidation were measured in this way. Tammann and Bochov have estimated the thickness of a film by direct weighing, and find it higher than that given by the colour, a discrepancy which they ascribe to absorption of air and water vapour.

F. P. Bowden and E. K. Rideal [56] have developed a novel method for the determination of the area of a contact catalyst, by measurement of the amount of hydrogen which must be deposited electrolytically to raise the potential of the catalyst a definite amount above that of the reversible hydrogen electrode. It is shown that 1/3000 of an atomic layer raises the potential by 100 millivolts for a plane surface such as mercury. The " accessible " areas of a number of catalysts (platinum, nickel, silver, and carbon) were determined in this way, and especially the effects of activation by alternate oxidation and reduction, cold working, and annealing. Constable [57] considers that the area measured in this manner would be smaller than that defined by "the envelope of the unimolecular film of hydrogen atoms, all in contact with each other and the surface, closely packed," whilst Bowden [58] gives reasons for supposing the " electrolytic " areas to be of greater significance.

The lack of uniformity of a catalyst surface, commented on by Langmuir, has given rise to the hypothesis of active patches, regarding which a number of different theories have been expressed. The number of surface actions which are known to be poisoned by small quantities of impurity is increasing rapidly (see E. B. Maxted and A. N. Dunsby [59] on the poisoning of platinum by arsenic in the oxidation of sulphur dioxide; also Constable [60]), but no further evidence for the existence of patches of great chemical activity, coupled with strong adsorptive fields on a surface, has been presented during the last year.

Constable [61] has reported on the theory of the centres of activity, and considers that the experimental facts of adsorption and catalysis can be explained quantitatively on the basis of strong specific fields of force caused by special configurations of atoms on the catalyst surface. Evidence from photoelectric data seems to suggest that active patches differ but little from normal surfaces in their intrinsic fields, and that structure, rather than field strength, is the criterion of active patches, if indeed they exist. Thus (Miss) J. Butterworth[62] has shown that the patches of Richardson and Young[13] can acquire the normal work function under prolonged illumination, and R. Suhrmann's[63] observation, that the emission from thin sheets of alkali metals rises with increasing potential at the red end, has been explained by B. Gudden[64] on the basis of local differences of potential of the order of 0·1 volt. Suhrmann[65] points out that this is in contrast with his suggestion of surface ionisation. The work of Bowden and Rideal cited above may be interpreted in a similar sense.

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[53] *Proc. Roy. Soc.*, 1928, [*A*], **119**, 196, 202; **A.**, 832; **117**, 376; **A.**, 106.

[54] *Z. anorg. Chem.*, 1928, **169**, 42; **A.**, 358.

[55] *Nature*, 1928, **121**, 351; **A.**, 375.

[56] *Proc. Roy. Soc.*, 1928, [*A*], **120**, 59, 80; **A.**, 1088.

[57] *Nature*, 1928, **122**, 399; **A.**, 1101.

[58] *Ibid.*, p. 647; **A.**, 1336.

[59] *J.*, 1928, 1600; **A.**, 849.

[60] *J.*, 1927, 2995; **A.**, 1928, 139.

[61] *Proc. Camb. Phil. Soc.*, 1928, **24**, 291; **A.**, 718.

A few observations on the physical structure of the catalytic interface are of interest. F. E. Smith[66] has examined the efficiencies of copper, nickel, their mixtures, and mixtures with alumina in the synthesis of water in carefully controlled conditions, and correlates the maximum efficiency with the least shrinkage on reduction of the hydroxides from which the catalysts are prepared, and with subsequent heat treatment. Smith supports Taylor's view of the catalyst surface, and considers that the reaction probably proceeds by the interaction of hydrogen molecules with activated oxygen molecules or atoms at points of greatest activity on the surface. E. Müller and K. Schwabe[67] measured the potentials of finely divided palladium, platinum, rhodium, iridium, ruthenium, and osmium while formic acid was being oxidised or decomposed on the surface of these catalysts, and found that only metals which could raise the pressure of adsorbed hydrogen on the surface to 1 atmosphere could assist the decomposition, whilst the other metals assist the oxidation. The potential measurements indicated that oxidation was dependent on the activation of hydrogen.

L. Duparc, P. Wenger, and C. Urfer,[68] with other workers, studying the oxidation of ammonia on metals of the platinum group, however, consider that the efficiencies as catalysts are determined by chemical rather than physical factors.

Kunsman[14] found no increase in the catalytic activity of thoriated tungsten over pure tungsten, molybdenum, or nickel in the thermal decomposition of ammonia, and considers the activity to depend on the constant A in the formula $K = Ae^{-E/RT}$.

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[62] *Phil. Mag.*, 1928, (7), **6**, 1, 352; **A.**, 931, 1068.

[63] *Naturwiss.*, 1928, **16**, 336; **A.**, 680.

[64] *Ibid.*, p. 547; **A.**, 808.

[65] *Ibid.*, p. 616; **A.**, 1068.

[66] *J. Physical Chem.*, 1928, **32**, 719.

[67] *Z. Elektrochem.*, 1928, **34**, 170; **A.**, 488.

[68] *Helv. Chim. Acta*, 1928, **11**, 337; **A.**, 487.

O. Eisenhut and E. Kaupp [69] have made an X-ray study of the iron catalysts used in the ammonia synthesis, and find maximal activity when the lattice structure is identical with α-iron, which is the essential constituent in all such catalysts, however prepared.

D. R. Hughes and R. C. Bevan [70] have carried out experiments on the union of oxygen and hydrogen on nickel wires in a rather novel way, examining the accommodation coefficients of the wire in pure hydrogen, oxygen, and their mixtures. They conclude that the wire is immediately covered with oxide, and that reaction takes place either at nuclei or at the nickel–nickel oxide interface, the latter being more probable for a thin film. B. Topley and J. Hume [71] find that the decomposition of calcium carbonate hexahydrate is autocatalytic, and they explain this from the point of view of an interface reaction, the formation of nuclei proceeding as the reaction progresses.

Experiments with contact catalysts on other reactions, both organic and inorganic, are too numerous even to mention. Particular attention, however, seems to have been paid to colloidal catalysts and metallised gels. Of the former class, mention may be made of the work of S. Liepatov [72] on barium and copper acetate colloids, of E. Biilmann and A. Klitt [73] on the reaction of $H_2(\text{gas}) \rightleftharpoons H^{\cdot}$ on colloidal palladium, of C. Marie and P. Jacquet [74] with gelatinated electrolytic copper, of A. Korolev [75] on esterifications with silica gel, and of F. Diaz Aguirreche,[76] who studied catalytic hydrogenations on platinum oxide, which was transformed to colloidal platinum. The use of metallised gels has been the subject of four papers by L. E. Swearingen and L. H. Reyerson [77] and one by V. N. Morris and Reyerson.[78] Reactions occurring at liquid–liquid interfaces are of interest in this connexion.[79]

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[69] *Z. physikal. Chem.*, 1928, **133**, 456; **A.**, 850.

[70] *Proc. Roy. Soc.*, 1927, [*A*], **117**, 101; **A.**, 1928, 27.

[71] *Ibid.*, 1928, [*A*], **120**, 211; **A.**, 1100.

[72] *Ber.*, 1928, [*B*], **61**, 45; **A.**, 250.

[73] *Z. physikal. Chem.*, 1927, **130**, 566; **A.**, 1928, 28.

[74] *Compt. rend.*, 1928, **187**, 41; **A.**, 850.

[75] *J. Chem. Ind. Moscow*, 1927, **4**, 547; **A.**, 637.

[76] *Anal. Fis. Quim.*, 1927, **25**, 411; **A.**, 1928, 172.

[77] *J. Physical Chem.*, 1928, **32**, 113, 191; **A.**, 252, 376; *J. Amer. Chem. Soc.*, 1928, **50**, 1872.

[78] *Proc. Indiana Chem. Soc.*, 1927, **36**, 203; **A.**, 1928, 488.

[79] See R. P. Bell, *J. Physical Chem.*, 1928, **32**, 882; **A.**, 848; G. Harker and R. K. Newman, *Proc. Roy. Soc. New South Wales*, 1926, **60**, 45; **A.**, 1928, 250; W. Fraenkel, E. Wengel, and L. Cahn, *Z. anorg. Chem.*, 1928, **171**, 82; **A.**, 717.

The general problem of homogeneous catalysis in solution, and in particular that of acid and basic catalysis, has been fully dealt with in the Discussion organised by the Faraday Society, and it would be superfluous to report on it again here. There remain a few papers on the theoretical side which are of interest.

R. E. Burk and D. C. Gillespie [80] consider the kinetics of molecules on a surface attached at more than one point, and calculate the rate of desorption from the probability of one or more link being broken; and the condition for singly or doubly attached molecules being desorbed at the same rate is also given. D. H. Bangham [81] applies an extension of Hooke's law to the condition in the interior of a solid when gases are adsorbed on the surface, and in the course of a very interesting paper he considers the strains imposed by the adsorbed molecules in some detail. He regards the sorbed molecules as distending the rigid coherent structure of the adsorbent, which thus becomes stressed and may even be distorted to such an extent as to allow free gas molecules to pass into the interior. More quantitative support for theories on these lines might prove very valuable.

Constable has endeavoured to develop a new mass-action law by introducing the condition that reaction takes place on centres at which the heat of activation is smallest, and some success is attained in those special cases where the intractable general equation can be simplified. In another paper,[82] the Reichinstein displacement principle for a bimolecular reaction at a catalyst surface is considered from the point of view of inelastic collisions on the solid surface.

Frenkel and Semenoff [83] have considered the parts played by collisions and heat radiation in activating and deactivating molecules, and the relation between the velocity coefficients of the two opposing reactions is obtained. These authors show how an analysis of the kinetics of a reaction can be made more than usually valuable.

In a rather different category are L. S. Kassel's two papers [84] on homogeneous gas reactions, in the first of which an expression is derived for the velocity of a unimolecular reaction at any pressure and is shown to fit the results obtained for the decomposition of azomethane. This theory is later extended by introducing quantised degrees of freedom, and the extended equation is used to account for the known data on nitrogen pentoxide : the agreement is good at moderate pressures, but less satisfactory at the lowest pressures. These two papers seem to be a definite step forward in this most disconcerting problem. (Frl.) G. Kornfeld's study [85] of the effective cross section of the gas molecule in chemical kinetics, which L. Nordheim [86] has shown to be a variable, may also be germane to this question. Kornfeld points out that in the case of water vapour catalysing the hydrogen–chlorine reaction, the minimum effective cross section of the water molecule is found to be 30 times the value obtained from the kinetic theory, so this effect must be much larger than was supposed.

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[80] *Proc. Nat. Acad. Sci.*, 1928, **14**, 470; **A.**, 847.

[81] *Phil. Mag.*, 1928, (7), **5**, 737; **A.**, 599.

[82] Constable, *Proc. Camb. Phil. Soc.*, 1928, **24**, 56, 307; **A.**, 252, 718.

[83] *Z. Physik*, 1928, **48**, 216.

[84] *J. Physical Chem.*, 1928, **32**, 225, 1065; **A.**, 372, 960.

R. H. Fowler [87] shows that in certain circumstances the deactivation target must be very large compared with the activation target, or expressed differently, that a very slow molecule, or one with exceptionally little energy, finds it very easy to bring about deactivation. L. S. Kassel,[88] in a more recent paper, considers that the collisional area cannot properly be regarded as variable, and he can arrive at no conclusion as to the mechanism of the decomposition of nitrogen pentoxide. Fowler thinks it probable that the radiation theory will have to be abandoned in favour of a theory of molecular interaction, and suggests that something in the nature of Heisenberg's resonance theory, which may be regarded as a collision process, should be adopted.

R. D. Kleeman [89] suggests a thermodynamic basis of catalysis as a result of his theoretical studies of the equation of state and the constant of mass action. Extending his results, he shows how a dense substance in contact with reacting gases which it may occlude can render the mass-action constant a function of the volume and masses of the constituents; and hence a catalyst may alter the constants of the reaction if present in more than appreciable quantities. R. Dubrisay [90] has considered the same effect in a slightly different manner.

The sixth Report of the Committee on Contact Catalysis, compiled by Burk,[91] contains critical reviews of most of the current theories in connexion with catalysis.

E. K. Rideal.
O. H. Wansbrough-Jones.

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[85] *Z. physikal. Chem.*, 1927, **131**, 97; **A.**, 1928, 104.

[86] *Z. Physik*, 1926, **36**, 496; **A.**, 1926, 654.

[87] "Statistical Mechanics," Cambridge University Press, p. 4, 1929.

[88] *J. Amer. Chem. Soc.*, 1929, **51**, 54.

[89] *Phil. Mag.*, 1928, (7), **5**, 263, 668, 1191; **6**, 195; **A.**, 263, 470, 937, 955.

[90] *Trans. Faraday Soc.*, 1928, **24**, 713; *J. Chim. physique*, 1928, **25**, 581, 658.

[91] R. E. Burk, *J. Physical Chem.*, 1928, **32**, 1601.

1929.

ATOMIC WEIGHTS.

Where the last figure of an atomic weight may be in error by several units it is given as a subscript figure. Where the last figure is given in ordinary type its error probably does not exceed one, or at most two, units.

Atomic number.	Name.	Symbol.	Atomic weight.	Mass-numbers of isotopes in order of intensity.
1	Hydrogen	H	1·0078	1
2	Helium	He	$4{\cdot}002_2$	4
3	Lithium	Li	6·94	7, 6
4	Beryllium	Be	9·02	9
5	Boron	B	10·83	11, 10
6	Carbon	C	$12{\cdot}003_6$	12
7	Nitrogen	N	14·008	14
8	Oxygen	O	16·0000	16
9	Fluorine	F	19·00	19
10	Neon	Ne	20·18	20, 22, 21
11	Sodium	Na	23·000	23
12	Magnesium	Mg	24·30	24, 25, 26
13	Aluminium	Al	$26{\cdot}97_0$	27
14	Silicon	Si	$28{\cdot}0_8$	28, 29, 30
15	Phosphorus	P	$30{\cdot}98_2$	31
16	Sulphur	S	$32{\cdot}06_5$	32, 33, 34
17	Chlorine	Cl	35·457	35, 37
18	Argon	A	39·94	40, 36
19	Potassium	K	$39{\cdot}10_5$	39, 41
20	Calcium	Ca	40·09	40, 44
21	Scandium	Sc	$45{\cdot}1_5$	45
22	Titanium	Ti	47·90	48
23	Vanadium	V	50·95	51
24	Chromium	Cr	52·04	52
25	Manganese	Mn	54·95	55
26	Iron	Fe	55·84	56, 54
27	Cobalt	Co	58·95	59
28	Nickel	Ni	58·69	58, 60
29	Copper	Cu	63·55	63, 65
30	Zinc	Zn	65·38	64, 66, 68, 67, 65, 70, 69
31	Gallium	Ga	69·72	69, 71
32	Germanium	Ge	72·60	74, 72, 70, 73, 75, 76, 71, 77
33	Arsenic	As	$74{\cdot}93_4$	75
34	Selenium	Se	79·2	80, 78, 76, 82, 77, 74
35	Bromine	Br	$79{\cdot}91_5$	79, 81
36	Krypton	Kr	82·9	84, 86, 82, 83, 80, 78
37	Rubidium	Rb	$85{\cdot}4_3$	85, 87
38	Strontium	Sr	$87{\cdot}6_3$	88, 86
39	Yttrium	Yt	$88{\cdot}9_3$	89
40	Zirconium	Zr	91·2	90, 94, 92, (96)
41	Niobium (Columbium)	Nb (Cb)	93·3	
42	Molybdenum	Mo	96·0	
43	Masurium	Ma	—	
44	Ruthenium	Ru	$101{\cdot}6_5$	
45	Rhodium	Rh	102·9	
46	Palladium	Pd	106·7	
47	Silver	Ag	107·880	107, 109

Atomic number.	Name.	Symbol.	Atomic weight.	Mass-numbers of isotopes in order of intensity.
48	Cadmium	Cd	$112{\cdot}4_0$	114, 112, 110, 113, 111, 116
49	Indium	In	114·8	115
50	Tin	Sn	118·70	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
51	Antimony	Sb	121·76	121, 123
52	Tellurium	Te	127·5	128, 130, 126
53	Iodine	I	$126{\cdot}93_2$	127
54	Xenon	Xe	130·2	129, 132, 131, 134, 136, 128, 130, 126, 124
55	Cæsium	Cs	$132{\cdot}8_1$	133
56	Barium	Ba	$137{\cdot}3_6$	138
57	Lanthanum	La	$138{\cdot}9_0$	139
58	Cerium	Ce	140·2	140, 142
59	Praseodymium	Pr	140·9	141
60	Neodymium	Nd	$144{\cdot}2_5$	142, 144, 146, (145)
61	Illinium	Il	—	
62	Samarium	Sm	$150{\cdot}4_3$	
63	Europium	Eu	152·0	
64	Gadolinium	Gd	157·0	
65	Terbium	Tb	159·2	
66	Dysprosium	Dy	$162{\cdot}4_6$	
67	Holmium	Ho	163·5	
68	Erbium	Er	167·6	
69	Thulium	Tm	169·4	
70	Ytterbium	Yb	$173{\cdot}_0$	
71	Lutecium	Lu	$175{\cdot}_0$	
72	Hafnium	Hf	178·6	
73	Tantalum	Ta	181·3	
74	Tungsten	W	184·1	
75	Rhenium	Re	—	
76	Osmium	Os	$191{\cdot}_0$	
77	Iridium	Ir	$193{\cdot}0_4$	
78	Platinum	Pt	195·2	
79	Gold	Au	$197{\cdot}2_1$	
80	Mercury	Hg	$200{\cdot}6_0$	202, 200, 199, 198, 201, 204, 196
81	Thallium	Tl	$204{\cdot}_3$	
82	Lead	Pb	$207{\cdot}2_2$	208, 206, 207
83	Bismuth	Bi	$209{\cdot}0_0$	
84	Polonium	Po	—	
85	—	—	—	
86	Niton (Emanation)	Nt (Em)	222	
87	—	—	—	
88	Radium	Ra	$225{\cdot}9_5$	
89	Actinium	Ac	—	
90	Thorium	Th	232·15	
91	Protoactinium	Pa	—	
92	Uranium	U	$238{\cdot}1_5$	

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